BAKERY PRODUCTS SCIENCE AND TECHNOLOGY

SECOND EDITION

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Bakery Products Science and Technology

Second Edition

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Preface to the Second Edition

Bakery products, especially bread, have a long history and they form an important part of the diets of humans around the globe. Bakery products are not only popular in traditional markets such as Europe, but they are also gaining popularity in emerging markets. For example, Euromonitor International recently reported that China's market for industrial baked goods was valued at US$25.4bn for 2013, up from US$19.6bn in 2012.

Meanwhile, today's consumers are increasingly conscious of health issues, so producing high-quality bakery products presents both a challenge and an opportunity. While there is no dispute that bakery products contain a high amount of carbohydrate and some may also contain gluten and high levels of fat and sugar, they can also be a source of wholesome food and balanced nutrients. Producing new types of bakery products or reformulating existing ones to increase their nutritional value or raise their nutritional profile is likely to remain a trend for the foreseeable future.

Since the publication of the first edition of this book in early 2006, progress in the science and technology of baking and bakery products has done much to address these and other challenges. Therefore, the second edition provides a timely update and expansion to the previous edition. The book consists of 42 chapters that are grouped into 7 parts:

1. Introduction to baking and bakery products;

2. Characterization and properties of important types of flours for bakery products, including those from wheat, rye, rice, barley, maize, sorghum, millet, and other grains;

3. Major baking ingredients such as water, yeast and other leavening agents, ascorbic acid and other redox agents, sugar and sweeteners, lipids, egg, dairy ingredients, enzymes, and other functional additives;

4. Science and technology of bakery production with dedicated chapters on mixing and dough making, fermentation, baking, and packaging. Also included are shelf-life prediction, process optimization and control, and sensory and nutritional attributes of bakery products. Specific issues such as rheology, browning, and functional bakery products are also covered;

5. Manufacturing of a variety of bread products including yeast bread, sourdough, frozen dough, par-baked bread, and steamed bread, as well as their quality control issues;

6. Other selected bakery products such as cakes, biscuits, pastries, pretzels, bakery products from unconventional flours, and dietetic bakery products; and

7. An overview of specialty bakery products from around the world as well as an in-depth analysis of bakery products from selected countries including China, Italy, Mexico, and Turkey.

Despite every intention to provide a comprehensive reference book on baking science and technology, we appreciate that it is not possible to claim that this book represents complete coverage. Nevertheless, we hope it serves as an essential reference on the latest knowledge and technologies for professionals in the baking industry, academia and government bodies,

as well as for undergraduate and postgraduate students in their study and research related to baking and bakery products.

We truly wish that you enjoy the book and find its contents informative and beneficial to your work, research, or study.

Weibiao Zhou and Y.H. Hui

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Part 1
Introduction

1

Introduction to Baking and Bakery Products

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Introduction

Bakery products, particularly bread, have a long history of development. Evidence from the most recent archaeological discovery indicates that baking practice may have started as early as 23 000 years ago (i.e. ~21,000 BC) during the Paleolithic Period (Piperno and others 2004). At that time, people discovered wheat and learnt to mix wheat grain meal with water and bake it on stones heated by fire. This gave birth to the first flat bread made by humans. During the period of 2600–3000 BC, yeast was used by ancient Egyptians to make fermented bread. Due to the high cost of milling, whole wheat and whole grain bread was generally consumed. White bread was also available, but limited only to groups of rich people. Since the 1900s, white bread has become common for everyone. Today, bakery products range in complexity from consisting of the simple ingredients of a plain pastry to the numerous components that make up a cake. The evolving of bakery products from the original plain and simple forms to the modern varieties with specific attributes and functionalities using sophisticated manufacturing technologies has been going hand-in-hand with the progress in many related fields of science and technology. For today's professionals, keeping abreast of the advanced knowledge in bakery products' science and technology is critical to continuously improve the productivity of current practice, identify the most important areas to direct limited research and development resources, and launch new competitive products into the market, as well as to predict future trends in the industry.

This chapter highlights the topics covered in this book using selected material from each chapter. Table 1.1 serves as a frame of reference for the discipline.

Table 1.1 Baking science and technology: a composite picture[a]

Materials of Baking Products
Ingredients from wheat
Wheat flour milling
Other wheat products
Ingredients from other grains
Rye
Rice
Barley
Sorghum
Corn
Oat
Millet
Soy
Yeast and chemical leavening

[a]Some of the listings in this table are inspired by Lai and Lin (2006).

Flours

Wheat flour

Wheat is the most versatile cereal due to the capacity of its storage proteins to interact and develop the gluten network, which forms the basic framework of many bakery products. Because there is a deep crease in the kernel, flour is extracted by a sequence of breaking, sieving, and size-reducing processes, known as the milling process. This process makes it possible to contemporaneously separate the bran and germ regions and to break the endosperm cells into a very fine product, suitable for rapid hydration and gluten development. Milling yield and flour refinement are closely related both to the milling conditions and the variety of wheat used. The latter highly influences the technological performance of the flour (measured by several instrument tests) and bread characteristics. As well as refined flours, increasing attention is being given to whole wheat flours that include the bran and germ fractions, which are presently considered to be by-products despite their richness in several bioactive compounds.

Wheat flour chemistry

The biochemistry of the main components of wheat flour (proteins, carbohydrates, and lipids) are presented and discussed with a focus on those properties relevant to the baking industry. As well as considering the composition and structure of each of the major macromolecules in flour, particular attention is paid to the interactions among the various flour components and to their modification in the various phases of baking-related processes. The role of water transfer issues is also considered, along with its modulation by flour components or by added ingredients.

Rye flour

Rye (*Secale cereale* L.) is a traditional raw material for baking in northern and eastern Europe. The flavor and structure of rye bread are quite different from those of wheat bread, and vary depending on flour type, other raw materials and ingredients, dough making process, baking conditions, and time, as well as the size and shape of the bread. Generally consumed as whole grain products, rye offers a good source of dietary fiber, phenolic compounds, vitamins, trace elements, and minerals. Rye bread has also been shown to have beneficial physiological effects, especially for glucose metabolism and satiation. Expanding research data strengthen the position of rye grain as an important raw material for healthy foods, and the potential for developing novel products is growing with the knowledge about its transformations during milling and baking processes.

Rice flour

Rice is one of the most consumed cereals, mainly as milled rice. However, several different value-added rice products have been developed prompted by the unique nutritive properties of this grain. Among all the processed rice-based products that are being launched, bakery products have received special attention. Nowadays, more people are attracted to wheat-free

foods because of health concerns or to avoid wheat in the diet. The chapter on rice gives a brief description of rice production and reviews the physicochemical characteristics of rice flours and their use in baking.

Barley, corn, sorghum, and other cereal grains

Developing countries with diets based on coarse grains continue to derive 70–80% of total food calories from maize, sorghum, and/or millet. In developed countries, the concept of using South American, African, and Asian traditional non-wheat cereals and ethnic grains as a template for wheat, wheat-free, and gluten-free based foods, matches the interest in westernized countries for exotic foods with their previously unappreciated extra nutritional value. Chapter 6 gives an update on the traditional and new uses in baking of major coarse grains worldwide. Special emphasis is placed on the challenges and opportunities of using maize, barley, oat, sorghum, and millet in composite breads. The evolution of the production, consumption, share of calories, and categories of use of individual coarse grains is revised, and the diversity of ethnicl goods and bakery products from coarse grains across the continents is presented. An overview of the advances in coarse grain-based baked goods based on scientific and technological progress and on their health-promoting effects is provided.

Baking ingredients

Water

The importance of water as a baking ingredient is overshadowed by its overwhelming abundance. The role of water in baking science is perhaps not fully appreciated by most of us, but all master bakers know that water plays a major role in the art and science of baking. The amount of water controls the quality, texture, taste, odor, volume, flavor, and the mouthfeel of bakery products. The art of baking involves using the optimum amount of quality water.

Nearly all foods contain water, while it is the major component in many foods. Even dry foods contain some water. If the baking process does not call for water as an ingredient, water is still involved, because it is present in some of the ingredients. Water reacts with the baking ingredients and evaporates when heated. Chapter 7 explores many facets of water with an emphasis on its role in baking.

Yeast

Saccharomyces cerevisiae has been used in the production of fermented cereal-based products since ancient times. Its domestication and large-scale propagation were key factors in the development of the modern baking industry. Here, the authors review how the long association of *S. cerevisiae* with bakers and yeast producers has affected its make-up and genetic characteristics. They also look into how the yeast industry has achieved the low-cost transformation of abundant feedstock, such as molasses, in to cell biomass of high technological quality, and how genetic improvement approaches could address the demands of consumers and producers of strains with optimized or novel properties. Finally, they discuss the possibility of using non-conventional yeast species as alternatives to industrial *S. cerevisiae* strains.

Chemical leavening agents

Leavening agents including yeast, other microorganisms, and chemical leaveners are important for their gas producing ability to give volume and crumb structure to a baked product. Chemical leaveners are interesting for their almost immediate action when applied in a recipe. The production of carbon dioxide is responsible for the fermentation/expansion of a dough or batter and is important for crumb structure. Crumb structure is the result of a certain "lightness" that is important for the properties such as volume, shape, flavor development, tenderness, and brittleness of a baked product.

Carbon dioxide is produced by yeast, other microorganisms (sourdough), and chemical leaveners. Each leavening agent has a specific characteristic that makes it suitable for use in some products. Each leavening agent also has its limitations. The working mechanism of chemical leaveners and acidulants are discussed in Chapter 9.

While carbon dioxide is the most important factor for leavening, other gases (ammonia gas), water as steam, and incorporated air (added during the mixing process) also play a role in the expansion of baked goods.

Chemical leaveners are a group of leavening agents, mostly inorganic salts, which when added to dough, either singly or in combination, react to produce gases. Carbon dioxide is the main leavening gas and is produced by either decomposition, where ammonium bicarbonate produces ammonia, water, and carbon dioxide in the presence of water, or by the reaction of an acidic salt and sodium bicarbonate in the presence of moisture and heat to form a salt, water, and carbon dioxide.

Ascorbic acid and redox agents

Ascorbic acid is commonly used as an improver in the baking industry and in some countries it is the only oxidation improver allowed. Other dough improvers include potassium bromate and azodicarbonamide to oxidize and sodium metabisulfite and l-cysteine to reduce gluten-forming proteins. The key change affected by such materials is the sulfhydral/disulfide reaction which plays an important role in the rheological properties of bakery systems. In Chapter 10, the effects of these materials are reviewed in brief. Enzymes are now used to replace or support the action of the traditional redox materials and the effects of selected enzymes in the production of bakery products is described.

Sugars and sweeteners

Sweeteners are important ingredients in bakery products. As well as providing a sweet taste, they also affect the fermentability, appearance, flavor, color, structure, and texture of the finished products. There are many choices of sweeteners available, and the type chosen depends on the degree of sweetness needed, its functions in the dough or batters, and the desired appearance or texture of the baked product. Marketing and regulatory issues must also be checked carefully, as they can vary in different countries. Sucrose is one of the most important nutritive sweeteners used domestically and in the food industry. However, as a response to public interest in low-calorie products, there has recently been a growing interest in sucrose substitutes. This is a huge challenge, due to the detectable losses in appearance, texture, flavor, and mouthfeel of the final food caused by sucrose reduction or substitution.

Fats and fat replacers

Chapter 12 focuses on the properties and functions of lipids as ingredients in food applications. Lipids may play a variety of roles in food systems depending on their application. Differences in the crystallization of fats may yield networks with altered macroscopic properties. Firstly, this chapter discusses the role of food lipids in various common baked-product matrices. The relationships between the microstructure and the macroscopic properties of lipid networks are then discussed, focusing on the roles of crystallization, polymorphism, rheological properties, microstructure, and processing conditions. Finally, strategies for the replacement of fats in baked products for the purpose of improving human health are discussed.

Eggs

Chicken egg is a multifunctional food material used in the preparation of many foods (salad dressings, meringue, cakes, and so on). Its multifunctional role originates from the differing

properties of the albumen and the yolk fractions, which are made up of protein constituents that differ in molecular size and structural flexibility. Egg constituents in food products may function as foaming, emulsifying, and/or gel network agents, thus contributing to the development of their unique sensory and rheological characteristics. In baked products, especially cakes, egg functional constituents contribute to product structure development and physical stability, with the extent of this contribution depending on the product type and the presence of other functional ingredients.

Dairy ingredients

Chapter 14 describes the effect of adding dairy ingredients to gluten-containing and gluten-free bakery products. The addition of dairy ingredients improves the nutritional quality of bakery products but alters the rheological behavior of dough and batters and the quality of bread, cakes, and biscuits. Furthermore, some dairy ingredients are used as substitutes for bakery ingredients such as eggs and fats. The behavior of dairy ingredients in bakery products depends on their composition, changes during the production process, and on their interaction with other components. The chapter describes the characteristics of milk and the changes that occur during the production of concentrated, dried, and fermented milks, cream, cheese, whey, and casein and whey protein concentrates. This is followed by a description of the role of dairy ingredients in bakery products.

Enzymes

Chemical additives are often used to obtain improved bakery products. As enzymes are natural and safe, food industries prefer to use enzymes as alternatives to synthetic chemicals. The enzyme-catalyzed reactions are substrate specific and take place under mild conditions. Different enzymes such as amylases, proteases, peroxidases, glucose oxidase, xylanase, laccase, lipase, and transglutaminase are used to improve dough and bread quality. Use of these enzymes in non-bread, wheat-based products is also increasing. A basic knowledge of enzymes is required for them to be used efficiently as ingredients. Also, enzymes should be sourced from a safe organism and be free of toxins. In Chapter 15, basic aspects of enzyme properties, some of the important enzymes used in the baking industry and their effect on flour constituents in improving functionality, and the use of enzymes in improving the functionality of some non-bread, wheat-based products are discussed.

Other functional additives

Functional additives have been used in the bakery sector for almost a century. Today the selection of emulsifiers, a wide range of enzymes, and oxidizing and reducing agents has been extended because of the evolution of bakery equipment and processing and because of an increased understanding of the complex mechanisms of their interactions with different constituents of flour and dough. The various additives are developed to compensate for variations in the processing characteristics of flours. They improve the machinability of dough, simplify the process, improve the quality of baked goods, and extend their shelf-life. Chapter 16 discusses oxidizing and reducing agents, vital gluten, emulsifiers, and also briefly mentions enzymes.

Baking science and technology

Mixing, dough making and dough make-up

It cannot be stressed enough that mixing is the most important stage of the entire baking process. If it is not done properly, it is not possible to correct it later. Therefore discipline is required. It is not easy to repeat exactly the same process every 12 or 15 minutes; however, it is necessary and of the utmost importance. Someone who wants to be proud of the quality of the product he has made must also be proud of the fact that he is capable of repeating the same process over and over again – and that is a real challenge. In Chapter 17, the factors that influence mixing are discussed: calculating the temperature of water, different kneading machines, the head and tail effect, and so on.

Fermentation and proofing

Fermentation in baking is mainly due to yeast and lactic acid bacteria. Their metabolic activities are responsible for the quality of the dough and hence for much of the quality of the final bakery products. Mechanisms during fermentation mainly include generation of carbon dioxide gas (promoting dough expansion), lactic acid (contributing to dough acidity), acetic acid (acting as antifungal compound), exopolysaccharides (involving dough viscosity properties), volatile compounds (acting as flavoring agents), and amino acids (involved as precursors of flavoring compounds). In addition, fermentation may cause some change in starch digestibility and the availability of minerals and vitamins. Consistent fermentation can be easier to achieve using starter cultures. To monitor the kinetics of dough expansion during fermentation, non-destructive testing has been developed using digital video cameras, magnetic resonance microscopy, X-ray tomography, and acoustic waves.

Baking

During baking, heat and mass transfer takes place in the dough simultaneously and interdependently, and involves four major changes:

1. Gases are vaporized as the temperature increases: the gas cell increases in volume provided that the cell wall retains gases and is deformable.

2. Starch gelatinizes as temperature increases to an extent depending on the local availability of water; proteins coagulate. These changes limit the dough extensibility.

3. The initial structure with closed gas cells separated by dough walls is transformed into a porous structure with interconnected pores, known as the dough–crumb transition.

4. Under the action of high temperatures at the boundaries, water vaporizes in the oven atmosphere. Depending on the product thickness, but also on baking conditions, this supports the formation of a dry, hard crust in the case of dessert or bread dough, and may also lead to complete drying in the case of biscuits and cookies.

These different changes do not occur sequentially but overlap and they are discussed in detail in Chapter 19.

Packaging and shelf-life prediction

Bakery products are popular and appealing due to their nutritional, sensory, and textural characteristics. However, these qualities can start to deteriorate immediately after baking leading to staleness, loss of moisture and flavor, and a limited shelf-life. Therefore, research has focused on the development of advanced packaging and preservation technologies and techniques for bakery products. Inherent overall product quality, as well as environmental storage conditions, influence the characteristics of bakery products and hence affect their acceptance. Thus, packaging materials, methods, and conditions for different bakery products, as well as the methodology for estimating and predicting their shelf-life, have been investigated.

Process optimization and control

Chapter 21 describes how the processing of baked products involves a sequence of processing stages that starts with mixing and ends with cooling. A structured process optimization study must consider all stages as linked because changes to any one processing stage will affect the other stages as a result of the interactions between stages. For example, increasing the proofing temperature will change the gas cell expansion of bread dough and also affect the baking process because of the changes this imposes on heat and mass transfer. Additional difficulties in optimizing the bread making process are the timings from the start of mixing to the end of baking and how to ensure that changes made to one stage are not compromised by another. These difficulties pose interesting challenges for the subject of process optimization.

Sensory attributes

The flavor of a cereal product is formed by a combination of the volatile and phenolic compounds, amino acids and peptides, sugars, and fatty acids, and their relative amounts significantly influence the perceived flavor. The flavor of native grain is mild, but by bioprocessing, such as sourdough fermentation, germination, and enzymatic treatment, or by extrusion or milling fractionation, the cereal product flavor can be modified as desired. In addition to containing fiber and bioactive compounds, whole-grain products that are beneficial to health must be tasty so they are attractive to the consumer.

Nutritional attributes

Wheat bread has been an important source of caloric energy and protein for the people of many continents for thousands of years and continues to be so. Bread, particularly white wheat bread, has recently been implicated as contributing to the chronic diseases associated with obesity, although in its whole grain forms it may also ameliorate these conditions. Chapter 23 focuses on the physiological impact of bread composition and processing on obesity, diabetes, and cardiovascular diseases. Recent research has suggested that chronic low-grade inflammation, due to the passage of intestinal bacterial fragments into the body, is a cause of chronic obesity-related diseases and perhaps initiates obesity itself. Cellulose, arabinoxylans, phenolic substances associated with fiber, resistant starch, amylose content, and processing affect digestibility, rate of absorption, intestinal tight barrier function, bile acid excretion, fat excretion, blood cholesterol, blood glucose, blood insulin, and insulin

resistance.

Browning

Bakery products have typical quality features that are diverse and depend on the particular product and its country or region of origin (for example, there are regional variations of the same product). Surface color is an important sensory attribute particularly associated with appearance, aroma, taste, and with the overall quality of bakery products. It has a significant effect on consumer judgment as color influences the anticipated oral and olfactory sensations because of the memory of previous eating experiences. Therefore, surface color plays a key role in the acceptance of the product by consumers, and it is often used to determine the end point of the baking process.

The formation of color in bakery products occurs during the baking stage (unless colored ingredients or colorants are being used), which is the scope of discussion in Chapter 24. This phenomenon is widely known as browning and is the result of non-enzymatic chemical reactions – the Maillard reaction and caramelization – that produce colored compounds during baking. The Maillard reaction takes place where reducing sugars and amino acids, proteins, and/or other nitrogen-containing compounds are heated together, while caramelization describes a complex group of reactions that occur due to direct heating of carbohydrates, in particular sucrose and reducing sugars. Because of the type of reactants and products involved in the Maillard reaction and caramelization, the importance of browning development is not only related to sensory aspects but also to nutritional properties. From this angle, the Maillard reaction impairs the content and bioavailability of amino acids and proteins, and it may be related to the formation of harmful compounds such as acrylamide and hydroxymethylfurfural (HMF). On the other hand, some reaction products are associated with positive nutritional properties such as antioxidant activity.

Functional bakery products

Consumers' demand for healthier food products that prevent nutrition-related diseases and improve physical and mental well-being has led to the accelerated growth of the functional foods market. Nowadays, the bakery industry seeks to improve the health attributes of their products using functional ingredients. The major areas of development involving functional foods are gastrointestinal health and immunity, prevention of cardiovascular diseases and cancer, weight control, insulin sensitivity and control of diabetes, and mental and physical performance.

Fibers, flavors, vitamins, minerals, bioactive compounds, prebiotics, and probiotics are some of the compounds used most frequently to add value to food products. These topics are explored in Chapter 25.

Rheology of bread and other bakery products

Chapter 26 introduces rheological terms useful for food scientists and technologists in understanding the rheological properties of bakery products that correlate with baking performance. The properties related to the deformation of bread dough and the flow of cake batters are characterized to obtain parameters either through fundamental approaches

involving large or small deformation testing or through empirical approaches using standard test methods. The physical transformations of dough and batters that occur during mixing because of the forces and deformations arising from the mechanical actions of mixing are described. Rheological parameters from different measurement approaches are analyzed and compared. The chapter highlights the problems of differing and mismatched test ranges and speeds, as dough characteristics are highly dependent on the stresses, strains, and strain rates applied.

Bread

Bread manufacture

Bread is a major food item for many people across the world. Varieties of bread, particularly as functional foods, have been developed to serve the needs of the consumer. Nonetheless, for almost all bread varieties, the bread manufacturing process mainly consists of mixing, fermentation and proofing, sheeting, molding, baking, cooling, and, if required, slicing. Each of the steps plays a unique role in the development of dough and bread towards the quality of the final product; therefore they all need to be carefully operated within a prescribed range. Advanced process control and automation systems should also be designed and implemented for bread manufacturing.

Quality control

Bread quality is very much an individual perception, and is therefore a contentious issue. Quality means different things to different people, and no two people share the same opinion about a particular type of bread. However, cereal scientists and technologists are able to identify certain characteristics for each style of bread and to determine the attributes that add to quality and those that detract from it. In [Chapter 28](#) the issue of bread quality is tackled from the European prospective, and the factors that are considered to be important in the range of bread types that are popularly consumed in the United Kingdom and the rest of Europe are examined.

Appearance is the first visual assessment of a loaf, and key factors include the volume (size) of the bread as well as the color – particularly that of the crust – and the shape of the loaf. The quality issues considered to be important differ for each style of bread. For example, a key factor for sandwich-type bread would be the uniform distribution of small-sized bubbles, which gives the bread crumb its characteristic appearance and the physical strength to allow butter to be spread over the surface. For French baguettes, it is the crisp, flavorful crust that contributes most to eating quality, paired with an open and irregular crumb. For these two bread types, the production methods are essentially the same; the process must create the appropriate number and sizes of gas bubbles in the dough and ensure that they survive during subsequent processing. The process of creating and controlling bubble structure therefore makes a fundamental contribution to bread quality, and this chapter deals with the key mechanisms of structure control available to the baker, as well details on the choice of ingredients, formulations, equipment, and processing methods that affect the quality of the final product.

Sourdough

Sourdough is a mixture of cereal flour and water fermented with lactic acid bacteria (LAB) with or without yeasts, and includes traditional sourdoughs and fermented cereal foods. The growth of LAB acidifies the dough and imparts a sour taste and odor, while yeast fermentation contributes to the aroma and leavening. Sourdough fermentation improves texture, enhances nutritional status, and extends the shelf-life of baked products and

fermented cereal foods. LAB cultures adapt to the acidic environment of sourdoughs by developing acid-resistant mechanisms associated with arginine catabolism, glutamate decarboxylation, and exopolysaccharide formation, as well as through thiol accumulation and beneficial interactions with the yeasts. Cereal is a suitable matrix for developing functional foods by fermentation with probiotics, biofortification, and glutamate bioconversion to bioactive γ-aminobutyric acid.

Frozen dough and par-baked bread

In [Chapter 30](#), frozen dough and par-baked definitions and technologies are discussed. Particular emphasis is paid to dough gas retention properties and the roles of yeast in frozen and refrigerated dough. The principles of formulation and production for frozen, pre-proved frozen and refrigerated dough are identified and discussed. The manufacture of par-baked products is considered.

When a product is baked, sold, and consumed locally within 24–48 h of production, changes to the product quality are limited. However, if the product is to retain its edibility for longer, then strategies which extend its shelf-life are required. An alternative to shelf-life extension strategies is to use technology to interrupt the standard industrial bread processes and use the intermediates for bake-off production at local sites such as village bakeries, railway and petrol stations, and retail baking environments. Freezing and par-baking represent the two most common means of achieving such aims. However, a major challenge for the primary manufacturer of frozen dough and par-baked products is that the ultimate product is only determined at final bake-off, when the conditions and practices used are not usually within the primary manufacturer's control.

Steamed bread

Chinese steamed bread is widely known as 'eastern bread' and has been consumed in its various forms for more than 1700 years. Although it originated in China, its popularity has spread to Japan, Korea, and Southeast Asia. Steamed bread is the staple food in the wheat growing areas of northern China. It may be consumed at all meals and is usually eaten hot. Dough for Chinese steamed bread is made from fermented wheat flour or blends of wheat and other grain flours. The product is cooked by steaming in a steamer. The most common types of steamed breads are either round or roughly cylindrical in shape with a white, smooth, shiny skin devoid of crust. Texture varies from dense to open and the flavor is dependent upon local tastes.

Like European bread, where one piece of bread dough can be used to make different forms of products such as pan bread, rolls, and buns, the same piece of steamed bread dough can be used to make different forms of steamed products such as steamed bread, steamed buns, and steamed twisted rolls. Steamed products can be made with and without fillings.

Traditionally, steamed bread is made at home by hand. Today, in cities, almost all steamed bread, buns, and rolls are made in small factories. These modern factories use mechanical mixing, sheeting, and even rounding. Therefore, in [Chapter 31](#), all topics on steamed products refer to products made using mechanical processing.

Traditional and specialty products

Cakes

For centuries cake-making has changed very little. The 16th century Spice Cake, the 18th century Nun's Cake, even the rich Pound Cake of the colonial days required long hours of labor. Old "receipts" read:

> ...take a half a peck of fine wheat-flour ... three pounds of refined sugar ... dry them by the fire ... take four pounds of butter, beat it with a cool hand, then beat thirty-five eggs, etc.

Later recipes called for smaller amounts, but the method of mixing was essentially the same.

There are a variety of cake products with a broad range of formulations. Ingredients, such as flour, have improved through processing; therefore, cakes contain higher levels of shortening, sugar, eggs, and milk. The modern cake is characterized by a sweet taste, short and tender texture, and pleasant flavors and aromas. Chapter 32 presents current science and technology in the manufacture of cakes.

Biscuits

The word biscuit is derived from the Latin *panis biscotis* meaning twice cooked bread. This is because the original process consisted of baking the biscuits in a hot oven and then drying in a cool oven. Biscuit has two meanings: (i) small round bread leavened with baking powder or soda, and (ii) any of the various small flat sweet cakes. 'Biscuits' is the original British word used to include small baked products (usually flat) based on wheat flour with various inclusions of fat, sugar, and other ingredients. The name 'biscuit' is synonymous with 'cookie' but the former is more comprehensive in meaning in the United Kingdom and Indian sub-continent and the latter in the United States. Wafer biscuits represent a special type of baked product because they are formed between a pair of hot plates and not on a baking band or wire as are most other types. Today, biscuits are a part of snacks, luxury gifts, dietary products, infant foods, and also come with the addition of many expensive ingredients, such as chocolate and cream. In general, biscuits are recognized as those products that are cereal based and baked to a moisture content of less than 5%. The cereal component is variously enriched with two major ingredients, fat and sugar. The ingredients and manufacture details for biscuits are discussed in Chapter 33.

Pastries

The origin of puff pastry and Danish pastry is thought to be the Turkish *baklava*. Baklava is a rich, sweet pastry made of layers of phyllo pastry filled with chopped nuts and sweetened with syrup or honey. It is characteristic of the cuisines of the former Ottoman Empire. Phyllo dough is a paper-thin sheet of unleavened flour dough used for making pastries. By adding yeast to the dough, puff pastry becomes Danish pastry.

In Scandinavia and in Denmark in particular, the term *Danish* pastry is not used. In these countries bakers talk about *wienerbrot* which literally means "bread from Vienna". In French, the term used for Danish pastry is *viennoiserie,* again referring to Vienna as the origin of

these products. In Austria itself it is called *plunder.*

It is generally thought that the croissant originated in France. While traditionally ascribed to the French painter and cook Claude Gelée who lived in the 17th century (the story goes that Gelée was making a type of very buttery bread for his sick father and the process of rolling the butter into the bread dough created a croissant-like finished product), the origin of the croissant lies in Vienna. The shape of the croissant is a crescent moon and was first made by the bakers of Vienna during the 1683 siege of their beloved city by the Ottoman Empire. They made a *plundergebäck* in the shape of a crescent moon to betray the position of the Ottoman army. Years later when the French queen Marie-Antoinette (1755–1793) visited Vienna, she fell in love with the product in the shape of a half moon or *lune croissant* in French, hence the name *croissant* in French.

It is important to understand that all these types of products (puff pastry, croissant, Danish pastry) are made by creating alternating layers of dough and fat by folding and rolling the dough. Chapter 34 explores the world of European pastries.

Pretzels

Hard pretzels were introduced to the United States in the 1860s at Lititz, Pennsylvania and have since become a very popular snack food. Pretzel is said to have had its origin when a 12th century monk rewarded children who recited their prayers properly. The crossed center of the pretzel form, legend has it, represented the folded hands of prayer. Pretzels are acknowledged as a healthy snack and are gaining popularity around the world.

Since the 1980s, significant advances have been made in automating pretzel production. Considerable improvements have been made to the equipment used in plants including high-speed mixers, pretzel dough cutter systems, automated pretzel forming machines, and pretzel ovens. Several patents have also been granted for new methods in hard pretzel manufacturing. Chapter 35 describes traditional and new methods in the production of pretzels.

Bakery products of unconventional flours

Unconventional flours from fruits, legumes, and tubers are used in the elaboration of bakery products, replacing different amounts of wheat flour, or in products without wheat flour such as gluten-free products. Unconventional flours are used in bakery products so that ingredients such as dietary fiber and bioactive compounds that are not available in wheat or maize flours are included. This can lower the consumption of digestible carbohydrates that increase the glucose level in the blood, and could therefore have health benefits. Bakery products normally contain a high amount of starch that becomes digestible due to the cooking process. The combination of wheat or maize flours with ingredients rich in dietary fiber, such as unripe fruit and legume flours, decreases starch digestibility. Additionally, fruits like unripe banana present a high level of resistant starch. Results obtained in the studies so far have shown a higher amount of resistant starch, dietary fiber, and bioactive compounds in bakery products with added unconventional flours from unripe fruits and legumes; additionally, the glycemic response of these bakery products was lower than the control samples. The use of unconventional flours is an alternative to produce functional bakery products.

Dietetic bakery products

Increased consumer income, improved consumer understanding of nutrition, and enhanced consumer expectations are changing attitudes to the role of diet in the lifestyle of individuals. Global health systems in developed and developing countries have begun to shift emphasis from dealing with infectious disease to managing the challenges presented by increases in mortality caused by chronic diseases including cardiovascular diseases, diabetes, and cancer . Therefore, in recent years, assessing the health consequences of food consumption habits has emerged as an important topic of inquiry.

Bakery products may be usefully adapted to increase healthier eating options for consumers. "We are what we eat" is an apt adage adopted by some consumers to inform their dietary choices. It is therefore important for bakers to also be conversant with the range of consumer preferences and dietary needs characterizing the present bakery products market.

In Chapter 37, bakery products that cater for the special dietary needs of consumers are introduced. The following dietary market opportunities are discussed:

- food intolerances (specifically gluten and lactose intolerance and allergy to eggs),
- bakery products that contribute to a healthier lifestyle (low-fat, low-sugar, and high-fiber products),
- bakery products required for specialized diet requirements (consumers with diabetes),
- bakery products for special religious diet requirements (Kosher and Halal),
- bakery products suitable for lifestyle choices (sports nutrition, vegetarianism, and veganism), and
- bakery products suitable for various demographics of consumers (children, women, and seniors).

Each section includes a discussion on the challenges that each dietary requirement will present to the baker or bakery technologist.

Examples of world bakery products

World specialties

The list of speciality bakery products, especially bread, in the world is endless and it would be impossible to describe all of them. Suffice to say that if there are five bakers in a town, there will be five different kinds of bread. This is because the secret of bread making does not only lie in the recipe but also in the way the product is actually made. The discussion in [Chapter 38](#) is limited to a number of products (and their production methods) that are distinct and well-known throughout the world, with some emphasis on Belgium.

Bakery products in China

It is unquestionable that China is a gourmet food paradise. Among countless delicacies in China, the delicate traditional baked foods are significant and play a very important role as either staple food or non-staple food. Wheat was cultivated in China about 5000 years ago. At first, the grains were eaten raw, but soon the art of grinding it into flour was learned. Even though wheat is a staple food grain in the West, the Chinese have developed many more ways to prepare it. This very wide variety of Chinese grain products, and their level of sophistication, is due to the many different methods of preparation and cooking that have been developed, including frying, deep frying, baking, steaming, and boiling. Dishes can be sweet, salty, soft, hard, crispy, spongy or flaky.

Italian bakery products

In Italy, popular tradition has led to the creation of different types of baked goods, both sweet and savory, whose origins come from the broad diversification over the centuries of crops cultivated in the different pedoclimatic conditions of the Italian peninsula and with the use of different fermentation procedures, including the sourdough process. A classification of Italian baked products based on different criteria – percentage of sugar in the formulation, texture, specific volume, and moisture content – is proposed [Chapter 40](#). The process cards of the most popular products are presented after a brief description of the different steps of the bread baking process. The products taken into consideration are different kinds of bread, produced from common wheat flour or remilled semolina by straight dough or sourdough fermentation, Neapolitan pizza, festivity cakes such as *panettone, pandoro* and *colomba,* and other traditional products of the different Italian regions.

Mexican bakery products

Mexico is probably the country that has the highest number of types of bread (around 1600) in the world. The Mexican bread industry can be considered as artisanal because small factories, including those inside supermarkets, produce fresh bread that is consumed immediately. Bread is also sold in baskets by people walking in the street or riding on bicycles. Mexican bread can be divided into two main kinds: salty and sweet. Salty bread is named "pan de labranza" with names such as "bolillo", "telera", "birote", "frances", and this kind of bread is the most consumed. There is a wide variety of sweet bread that is consumed

during breakfast and dinner. There are diverse kinds of bread such as "pan de muerto" and "rosca de reyes" that are prepared for festivals or special dates. The industry of Mexican bread and the types of products is a creativity that continues from generation to generation.

Bakery products in Turkey

Turkish cuisine is full of some amazing food components with which to spoil your taste buds. However, no matter where you go in Turkey and whatever it is that you eat, you will find one thing to be a constant part of the meals, and that is bread. Turkish bread is consumed not only for breakfast, but also with all meals at all times of the day. This is why almost every household either bakes its own bread or sends its dough to a communal bakery. Bread baking is such an integral part of the Turkish lifestyle that every household must have its own baker who is an expert at making the bread. The foundation of Turkish food is, if anything, dough made of wheat flour. The original white bread that is used in Turkey is called ekmek and flat bread is known as pide. There are other types of bread such as simit, with sesame seeds, and manti that has much in common with ravioli. There is a whole family of foods that are made out of these types of bread and are categorized under the name borek. These varieties of bread are eaten for breakfast as well as for snacks and they also accompany most of the daily meals. These versatile pieces of bread can be sliced, filled, fried, baked, toasted, grilled, and prepared in many inventive ways. The Muslims of the Ottoman period believed bread to be one of the earliest forms of cuisine dating back to the time of the Prophet Adam, and bread is still held as one of the simplest and most honorable foods to eat. Taking their inspiration from this very basic food, they make bread a big part of their daily lives. Some would argue that there is no bread on Earth that tastes like Turkish bread, and you have to eat it to realize how good it actually is.

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Part 2
Flours

2

Wheat Milling and FlourQuality Evaluation

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Overview

From the very beginning, humans realized that wheat was the most "versatile" of cereals. Although barley and rye could provide a workable dough, only wheat could be successfully transformed into foods that were highly diverse in their structure and palatability, such as bread, numerous other baked products, and pasta.

The essential process for obtaining all those foods is to break and grind wheat kernels and extract flour, that is, to mill the kernels. Milling, in fact, makes it possible to separate the main region of the wheat grain, the starchy endosperm – rich in technological functional compounds – from the bran and germ. At the same time, milling breaks down the endosperm into a product of fine particle size. When water is added, the huge surface of the flour particles provides a homogeneous, complete, and almost instantaneous hydration of the protein macromolecules, the first and essential phenomenon for dough formation and development.

The milling systems used today in modern industrial mills are obviously very different from those used by our ancestors thousands of years ago in the Middle East (the Fertile Crescent). Here wild wheat species were present and led to the spontaneous selection of mutants, which later evolved into modern domestic wheat (Brunckhorst 2006). The first attempts at milling gave flours rich in bran parts that had a low bread-making quality (*low milling processing*). This problem was overcome with the introduction of new machinery in the 1800 s, some specializing in grinding grains (roller mill) and others in sifting the crushed material (sifter and purifier), in sufficient numbers and succession to produce refined flours (*high milling processing*) (Madureri 1995). Since then, white refined flours have provided breads with higher sensorial properties, especially for softness, color, and flavor of the crumb.

Today, flour quality is no longer judged by its extraction flour yield and its degree of refinement. Other considerations must also taken into account such as hygiene, health, and safety (absence of chemical residue and microorganism contamination responsible for the production of toxins), technological properties (which may extend over a wide range according to the end-use of the flour), and the presence of high levels of nutritional compounds, in which wheat is naturally rich. All this, of course, without forgetting the economical aspects of the process. For this reason, the miller, whose trade until just a few decades ago was traditionally passed from father to son, must nowadays not only have considerable specific experience allowing to choose the best processing conditions to suit the characteristics and origin of the grain to be milled, but also have a knowledge of food science, chemistry, mechanical engineering, computer science, and economics. In short, the art of the miller has today become a science.

Wheat, a raw material of choice for bread and bakery products

The choice of ingredients is of fundamental importance for obtaining a leavened product that will satisfy the customer's expectations.

The property that makes wheat unique is the ability of its proteins to form viscoelastic dough. In other words, wheat dough has unique and particular rheological properties that enable the mass to be stretched and deformed without rupturing, as discussed later. At the same time, the dough is elastic and tenacious, capable of maintaining its assigned shape even when subjected to physical stress. After baking, gluten proteins lose their viscosity, assuring the maintenance of the final shape. The reason for wheat's peculiar and versatile behavior is not due to quantitative differences. In fact, the protein content of the numerous varieties of wheat is quite variable, from 9 to 16% of the weight of the entire grain (Chung and others 2003; Delcour and Hoseney 2010). This variability practically coincides with that of other cereals.

The technological superiority of wheat is due to the more complex differences of quality that can be observed, especially at the protein fraction level, as discussed in detail in Chapter 3. It is the only cereal to have storage proteins (gliadins and glutenins, together representing about 80% of the entire protein content) characterized by a particular amino acid composition. They are generally classified according to molecular weight (MW), solubility, and conformation. The storage proteins have a high percentage of glutamic acid (equal to about a third of all the residual amino acids and present as glutamine) and proline, and with a small quantity of lysine (Shewry and others 2009). Such a composition is responsible not only for the low biological value, but also for allowing protein–protein interactions that lead to the formation of gluten, a three-dimensional network that is continuous and homogenous throughout the dough mass.

Wheat grain: structure and composition

The wheat grain or kernel (Figure 2.1) – botanically named *caryopsis* – is a particular dry fruit, not opening at maturity, where three main regions are easily recognizable. On the outside, the fruit coat (or *pericarp*), contiguous and closely adherent to the *seed coat*, surrounds and protects both the *embryo*, or germ – the life-giving part of the seed – and the *endosperm*, the larger part of the kernel. The storage macromolecules, starch and protein, are tightly packed inside the endosperm cells. The organization of the caryopsis is common to all wheat species (hard and soft wheat, durum wheat, and so on) and to all other cereals. Nevertheless, wheat grain (together with barley and rye) differs as it has a deep longitudinal *crease* (or furrow) in the ventral side, which extends nearly to the kernel center.
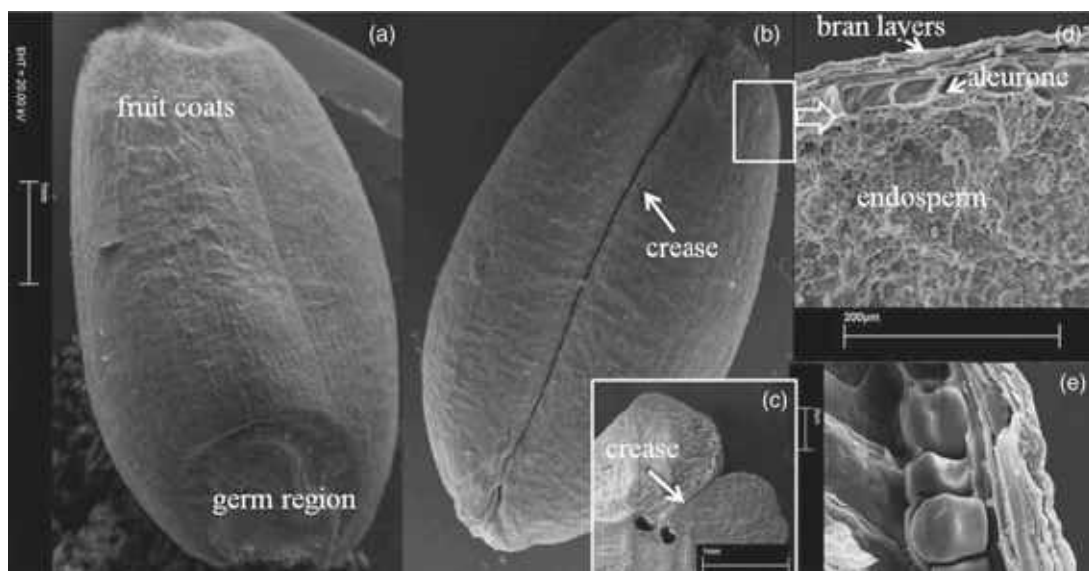
Figure 2.1 Scanning electron microscopy images of wheat kernel: (a) dorsal, (b) ventral, and (c) transverse section of kernel showing the crease; (d) and (e) details of the cross-sections showing the endosperm, the aleurone, and the bran layers.

Each kernel region exhibits a distinctive morphology and composition that fulfill its special functions (Table 2.1). The numerous peripheral layers provide a strong physical barrier, assuring protection against pests. Moreover, they are involved in water exchanges between the seed and its surroundings (Bechtel and others 2009). Consequently, every layer has lignified thick-walled cells, made up of different non-starch polysaccharides, minerals, and trace elements, while the cells of contiguous layers are each oriented in orthogonal directions.

Table 2.1 Composition[a] and specific weight of wheat kernel regions

	Fruit coat	Seed coat	Aleurone	Endosperm	Germ
Kernel g/100 g dm	10	2	8	82	3
Starch and soluble sugars g/100 g dm	14–16[b]	9–11[b]	10–14	80–85	19–21[b]
Proteins g/100 g dm	10–14	13–19	29–35	8–14	36–40
Lipids g/100 g dm	1–3	3–5	7–9	2–3	13–17
Non Starch Polysaccharides g/100 g dm	60–74	53–63	35–41	1–3	20–24
Ash g/100 g dm	3–5	9–15	5–15	0.5–1.5	4–6
Specific weight kg/m^3	180–260[c]		160–260[c]	1350–1400[d]	–
Milling fractions	Bran and middlings		Bran and red dog	Flour	Germ meal

[a] Adapted from Lucisano and Pagani (1997).

[b] The amount refers to soluble sugars.

[c] Adapted from Posner (2009).

[d] According to Dobraszczyk and others (2002).

The germ consists of two main parts: the embryonic axis that will give the future plant and the scutellum, a region with nutritive elements for the shoot. The germ, therefore, has a high percentage of sugars, soluble proteins, fats, vitamins, and minerals, but no starch or gluten is present.

The third region, the endosperm, represents about 80% of the whole grain's weight and also consists of two parts: the aleurone layer, formed by cubic cells, and the starchy endosperm (Figure 2.1). Due to its composition (high protein, lipid, sugars, and ash content, as well as vitamins and phytate), the aleurone layer spontaneously merges with bran during milling. The cells in the starchy endosperm have varying shapes, sizes, and wall thickness. In particular, in the more internal part of endosperm, the cells are thin-walled, with a higher starch content compared with the outside region (Bechtel and others 2009). Scientific and technological interest was mostly focused on the latter until the beginning of this millennium (Poutanen 2012), because it was made into flour, the main raw material for bread and pasta products. As over-consumption of highly refined and highly caloric foods had been strongly related to the "metabolic syndrome" increase in the western world (Shewry and others 2012), attention is now increasingly focused on bran and germ as sources of many bioactive compounds and phytochemicals. Many projects and research programs are now dedicated to the possibility of exploiting milling by-products in both traditional and new foods (Doblado-

Maldonado and others 2012; Delcour and others 2012).

Defining wheat quality: classification and grading

The different species of wheat (14 species are grown all around the world) (Wrigley 2009) are classified according to the number of chromosomes into diploid wheat (14 chromosomes, e.g., einkorn wheat), tetraploid wheat (28 chromosomes; e.g., durum wheat and emmer wheat) and hexaploid wheat (42 chromosomes; e.g., common or bread wheat). Presently, about 30 000 varieties are known, of which about 1000 are of commercial interest. In any case, each year a huge number of new varieties are developed by crossing and selecting procedures to meet various agronomic, nutritional, and technological requirements. In this chapter, we focus on common wheat (*Triticum aestivum*), as it represents the main species cultivated throughout the world and the source of flour for bread making.

The parameters of wheat quality

Due to their wide variability, trading, and utilization, harvested crops are necessarily based on classification systems, suitable for describing the "wheat quality" grade of the product. The term "quality" is often used in a very broad sense to define the overall potential for wheat to be successfully transformed into certain end products. The grading activity is carefully carried out by each country that produces and exports wheat: further information about the criteria and standards adopted for grain classification, as well as the classes and the range of each quality parameter are provided by dedicated Governmental Institutions, Agencies or Commissions (Table 2.2).

Table 2.2 Evaluation of wheat production in the main producer countries

Country	Wheat production (1000 t)[a]	Website	Number of classes
USA	54 000	www.usda.gov www.uswheat.org	6
Canada	25 000	www.grainscanada.gc.ca	14
Australia	29 000	www.wea.gov.au	6
China	90 000	www.chinagrain.gov.cn	9
India	72 000	www.icar.org.in	5
Russia	35 000	www.rusgrain.com	6
France	35 000	www.international.inra.fr	4
Germany	19 000	www.mri.bund.de	5

[a]Data related to 2010–2011 harvest.

Despite the differences between countries, there are some common standards for satisfactorily indicating wheat soundness and safety for describing a grain's aptitude to be milled to give a high yield and a high quality flour. Nevertheless, each operator in the wheat chain complies with specific quality criteria according to his position in that chain (Figure 2.2). It follows that the parameters used to express the quality of the wheat are not the same

at all points of the chain, and the common parameters may differ in importance. Moreover, the end use quality of wheat is related not only to genotype but also to environmental conditions (soil type, climate conditions). Consequently, the end use quality can change from year to year. This and further discussion here are not intended to be an exhaustive description of the indices currently proposed and used to express the quality of the crop (see the sites indicated in Table 2.2), but are intended to illustrate its complexity and its critical points.
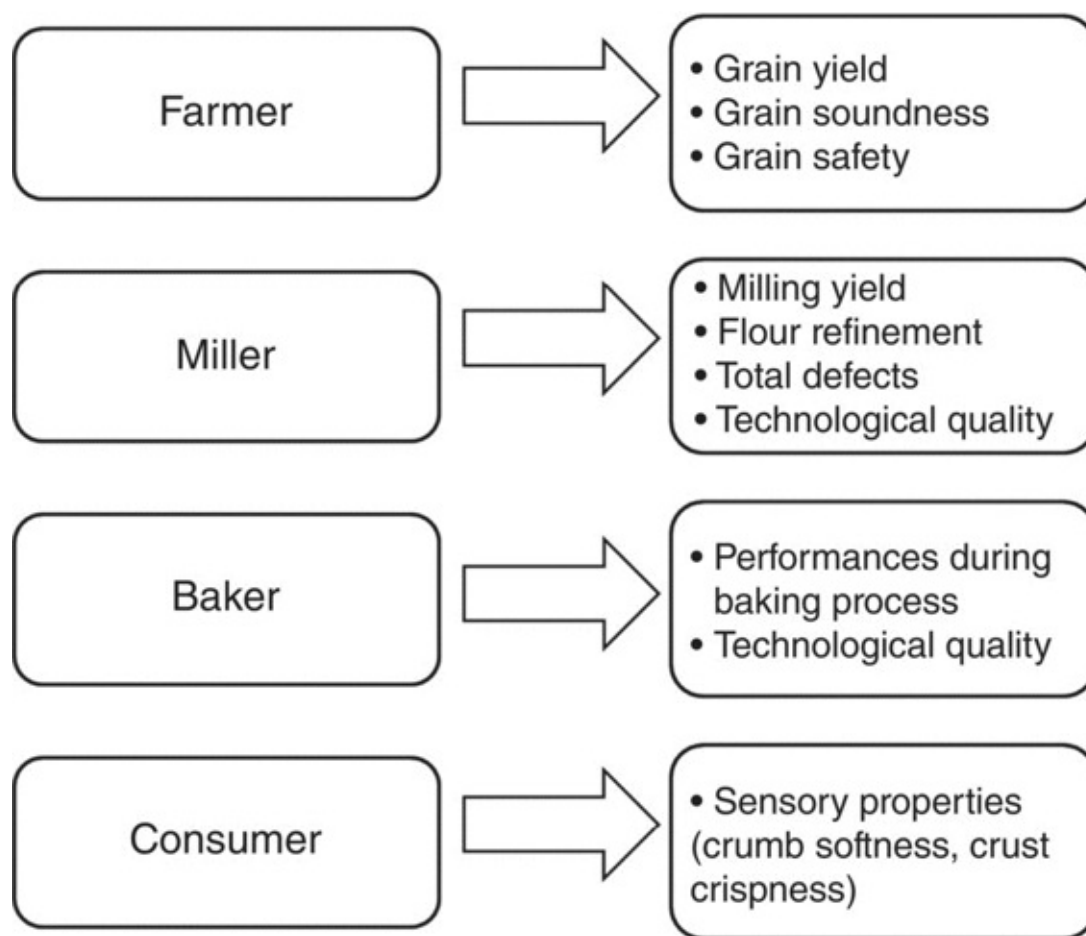
Figure 2.2 Criteria used for wheat quality assessment according to the position in the wheat chain.

The concept of quality for the farmer and during wheat storage

The concept of quality for a farmer is linked to a good germinability of the sown grain and to a sound and undamaged harvest, free from sprout damage, disease, and insect pests, that is "defects", and a moisture content assuring safe storage (generally, lower than 12%) (Posner and Hibbs 1997). A farmer is paid more money for harvested wheat exhibiting these quality characteristics.

During the greatly variable wheat storage period, control of the temperature and moisture of the kernels as well as the air are of the greatest importance. Together, these variables can greatly influence not only the respiratory activities of the kernels, but also insect and microorganism attacks, with dramatic consequences for product safety and end-use characteristics. Moreover, as demonstrated in the 1950s, extreme moisture (> 15%) may also induce germination phenomena (Zeleny 1954). Kernels exhibiting sprout damage have high level of α-amylase, which has little effect on the wheat milling quality, but greatly affects bread making and bread quality. In fact, a higher α-amylase activity, results in quicker starch

hydrolysis during the bread-making process. The fast production of sugar and dextrins induces stickiness in the dough, worsening the handling properties. The presence of sprouted kernels is usually provided by measuring the amount of α-amylase, by means of the Falling Number (FN) System (AACCI 2004, Method 56–81.03; ICC 2001, Standard 107/1).

The concept of quality at the mill

The quality criterion for the miller ([Figure 2.2](#)) is closely linked to the high yields obtained to maximize profits since, at present, flour commands a higher price than its by-products (bran, middlings, shorts, germ, and so on). In particular, the potential grain yield depends largely on the ability of the varieties to adapt to different (both favorable and unfavorable) environments and to exhibit high resistance to biotic and abiotic stresses. Thus, grain soundness and yield stability represent the major breeding goals for the development of new wheat varieties.

To obtain the maximum milling yield, millers ideally look for a wheat that is clean, uniform in size, and free from any contamination and physical or weather-induced damage, representing different types of *defects*. In reality, millers have to deal with wheat that may vary considerably in quality between shipments because of differences in variety, growing areas, and storage conditions (Marshall and others 1986; Carson and Edwards 2009). A standard of milling quality universally accepted by the milling industry is *test weight*, obtained by weighing the grains which fill a cylinder of fixed volume and expressed in units of lb/bu or kg/hl (Pomeranz 1987). Test weight provides a measure of the bulk density and compactness of the grains. It is greatly influenced by environment, kernel moisture, and protein content, as well as by kernel shape and size (Chasseray 1991). For this reason, a minimum value for test weight is generally required as primary specification in wheat grading and classification.

Thousand kernel weight (TKW) is the weight in grams of 1000 kernels and provides a measure of grain size and density. Test weight and TKW measure different features of the grain. While the former can be a reflection of the soundness of the grain, and therefore a high test weight may be expected when the grain is sound and undamaged due to good weather conditions, kernel weight will be a measure of average kernel size and thus larger kernels, resulting from correct grain ripening, are expected to have a greater endosperm to bran ratio (Chasseray 1991).

Grain *hardness* (AACCI 2004, Method 55–30), a parameter strongly linked to genotype, represents another important aspect of quality, being directly related to the force required and the energy consumed during grinding and milling. As it strongly affects grain tempering and milling performances, hardness represents a determinant parameter in creating homogeneous grain batches. Hard kernels are more resistant to reduction in size than soft kernels and require more energy to be crushed, but an overlap between the two classes still remains (Posner 2009). The textural differences between hard and soft wheat are determined by the presence of specific low molecular weight (LMW) proteins, the puroindolines (Morris 2002). The presence of these LMW proteins, occurring in soft varieties, promotes a weak adhesion among the starch granules and the protein matrix, favoring endosperm breakage (Barlow and others 1973; Greenwell and Schofield 1986).

Chemical characteristics (moisture, protein, and ash content) of wheat are not generally included in grading standards, but they are universally reputed to greatly influence the

technological quality of wheat. *Moisture content* (AACCI 2004, Method 44–19; ICC 2001, Standard 110/1) is very important to millers when buying grain lots. The percentages of other components, such as protein and starch, and test weight are inversely related to the moisture content (Troccoli and others 2000). The latter is therefore used for calculating the price of the product in the international market. This aspect has to be considered when comparing lots of grain from various countries. As already discussed, moisture, when too high, strongly influences spoilage and deterioration phenomena during storage (Bailey 1992). On the other hand, if the wheat is too dry, the miller would have to use a two-stage tempering process to prepare the wheat for milling, thus adding time and expense. Despite the strategic role assumed for safe storage and its economic and technological implications, at present there is no moisture level accepted worldwide as a basis for expressing quality characteristics (Posner 2009).

The *ash content* of wheat is the mineral residue remaining after incineration of the sample (AACCI 2004, Method 08–12.01; ICC 2001, Standard 104/1). This parameter is carefully measured as it can affect milling yield. The inclusion of some milling fractions could give an excessive ash value in the end flour.

The *protein content* of wheat can vary considerably from 9 to 16% of the weight of the entire grain; this variation strongly depends on the wheat variety, the growing conditions, the soil fertility, and the fertilizer inputs, particularly nitrogen (Carson and Edwards 2009). As is well known, the amount of protein strictly influences the end use of the flour. Generally, high protein content is associated with high gluten content and the ability to form a strong dough– best for bread making, especially when long leavening steps are required (Pagani and others 2010). Thus, the blending of different wheat varieties (often using imported wheat) allows the miller to create wheat mixtures with improved end-use functionality, and to supply flour types with constant protein quantity and quality. The protein amount is determined as nitrogen (with a conversion factor of N * 5.7) by the Kjeldahl method (AACCI 2004, Method 46–16; ICC 2001, Standard 105/2) or by the automatic Dumas combustion method (AACCI 2004, Method 46–30; ICC 2001, Standard 167).

Millers also have to meet the flour specifications demanded by their customers. According to the final destination of the products (industrial, commercial, or retail), the type of product (fresh or frozen dough, partially of fully baked, and so on), the formulation of the product, and the technological process adopted, the main factors to be considered are protein content, dough strength, water absorption, mixing properties, and Falling Number (Carson and Edwards 2009).

The concept of quality at bakery

For the bakery industry, a superior quality wheat has the technological capacity to form a cohesive and homogenous dough, as well as the ability to retain the gases produced during fermentation that are responsible for the textural and sensorial properties of bread and baked-products (Figure 2.2). Thus, the contribution of protein is a determinant for quality. Protein content is a fair indicator for flour applications (low-protein wheat is used for pastry, cakes, and cookies, and high-protein wheat is used for bread and blending purposes) (Pomeranz 1987; Carson and Edwards 2009), but the evaluation of *protein quality* makes it possible to improve the conditions of the baking processes. The numerous rheological approaches used for this purpose are described here.

The concept of quality for consumers

The high-quality breads and cakes preferred by consumers in North America or in Northern Europe differ significantly from those preferred by consumers in Mediterranean countries (Carson and Edwards 2009; see also Chapter 40). Nevertheless, development in volume – the *specific volume* (expressed as the ratio between volume and weight of bread) – and the distribution of *cell size* represent physical characteristics that are universally used for defining the quality of bread (Pyler 1988). At the macroscopic level, these indices show the structure of the crumb cell (percentage of alveoli in the total volume, the distribution of coarse and fine alveoli, and so on) and, together with moisture, represent the complex result of the interaction between the properties of the raw materials and the conditions applied at each phase of the bread-making process (Pagani and others 2010).

The dry milling of wheat

About 70% of the production of wheat worldwide is used for food (www.fao.org), mainly in the bakery industry (both for bread and other bakery products). It is estimated that approximately 350 million tons of flour are produced and transformed into bread and bakery products each year (De Bry 2006). This use has an essential preliminary step: the milling process.

The principle on which current industrial wheat milling is based is quite different from those principles applied in both the distant and recent past. The first attempts at flour production date back to the Neolithic era and consisted of grinding grains with stones, and later progressing to mortars and pestles (Webb and Owens 2003). About 5000 years ago (the Bronze Age), the saddle stone was introduced, as testified in Egyptian inscriptions and drawings. Milling with millstones is more recent (even though it dates back to 1000 BC) and continued to be used until around 1850, and is still present in some traditional processes. The first mills were powered by hand or by working animals; watermills and windmills were not introduced until much later (Madureri 1995). Two overlapping components were present in all types of millstones: the stationary base or bedstone and the mobile runner stone, both made of very hard stone. As well as taking advantage of the natural roughness of the stone, the surface of the millstone was worked with channels and furrows of different shapes (Figure 2.3). During rotation, the kernel was ground between the two stones and the ground material collected at the bottom of the bedstone. Even though the first attempts at milling (using mortar and pestle and millstones) crushed the grain effectively, these processes only partially removed the bran and germ from the endosperm.

Figure 2.3 Millstone (courtesy of Molino Quaglia S.p.A.).

The milling process was revolutionized during the second half of the 19th century with the introduction of cast iron roller mills (Madureri 1995) and the belief that progressive and delicate grinding actions, each alternated by sieving and sifting the ground material, would give a greater yield and a better separation of the bran (Dobraszczyk 2001).

Objective

The objective of this process is twofold as it isolates the starchy endosperm (that is, the area containing the gluten proteins and the starch granules) from the germ and from the pericarp and seed coats (that form the bran and other by-products). This result can be satisfactorily achieved due to the differing macrostructure, microstructure, and composition of the three regions which give them particular physical properties. The amount and the specific weight of kernel components (Table 2.1) especially influence the behavior of the three regions during

the different passages of the milling process, making their separation easier. At the same time, milling reduces the granulometry of the endosperm to values of less than 150–200 μm for flour from common wheat grain and 500 μm for durum wheat flour. The fine granulometry of flour gives a better workability and contributes to its transformation into palatable and appetizing food.

The removal of the bran parts not only improves the hygienic characteristics of the flour (the peripheral parts of the grain are contaminated with both chemical residues and biotic contaminants) but also its technological characteristics. The presence of non-starch polysaccharides and enzymes, abundant in the bran regions, are associated with a general worsening of the rheological characteristics of the dough as underlined by Katina (2003) and recently by Doblado-Maldonado and others (2012). Even the separation of the germ has a valid justification since this oil-rich part can easily turn rancid and compromise flour storage and shelf-life (Paradiso and others 2008). A short shelf-life is not acceptable in the present global market. A number of recent improvements to the milling process have been made to obtain a satisfactory compromise between the advantages and disadvantages associated with the removal of the bran and germ parts, as further discussed later.

In general, milling is much more complex than mere grinding. The particular morphological structure of the wheat grain has led to the development of a unique grinding process, different from a mere abrasion step, that effectively removes the majority of bran layers and separates the flour by "extraction" from the grain core. The process must therefore include operations that first "open" the grain. Then, proceeding from the inside towards the outside, the endosperm material is recovered using a repeated sequence of size reduction and separation stages, leaving the more external areas (bran, aleurone layer, and so on) as residue and therefore denominated "tailing products". This procedure, which fully justifies the definition "flour extraction yield" (Webb and Owens 2003), is the only solution for preventing the passage into the flour of the bran layers "hidden" in the furrow, which represent 25–30% of the total bran (Posner 2000).

The physical separation of the three main areas is made possible by their differing composition, but the detachment of the endosperm from the bran is not quantitative, since parts of the endosperm are lost in the milling by-products and a small percentage of bran fragments are inevitably present in the flour. The milling process, therefore, must make it possible to reach a compromise between the *extraction yield* (expressed as quantity of flour produced from 100 parts of processed wheat kernels) and the *refinement degree* (expressed as the accuracy of bran elimination). These parameters are inversely correlated (Freund and Kim 2006), but both are important for the cost effectiveness of the process and for the technological and nutritional properties of the flour (Rosell 2003).

Current technology may be subdivided into the following four stages: (1) receiving, precleaning and storage of the incoming wheat; (2) blending, cleaning, and conditioning; (3) milling; (4) storage of the flours produced (Figure 2.4). To produce the wide range of flours the bakery industry needs, the miller must have a precise knowledge of both the physical and chemical characteristics of each lot of wheat incoming into the mill and be able to segregate the wheat according to its hardness and protein characteristics. Just before milling, the miller will create the blend which makes it possible to produce a certain number of basic flours. The types of flours may be expanded not only by blending the basic flour types to acquire the desired chemical and technological attributes, but also by adding various enhancers to the

basic flours, thus satisfying the rheological, chemical, and nutritional requirements of the customer.
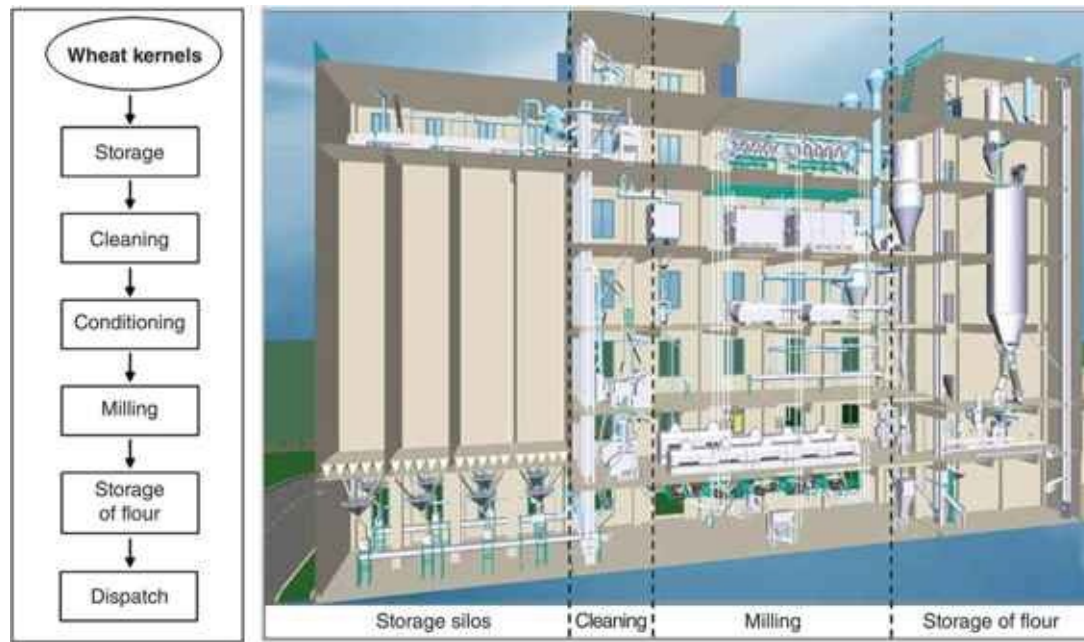
Figure 2.4 Simplified flow-sheet (left) and lay-out (right) of wheat milling (copyright and courtesy of Bühler Group).

Grain storage

The grain stored in bins represents a complex ecosystem (Dunkel 1992). As stated by Fleurat-Lessard (2004), storage has three main goals: (1) the assessment of the quality of each grain load delivered by the farmers in order to identify quality grades; (2) the preservation of the original properties and composition of freshly harvested grain; and (3) the permanent supply of the first processing industries with homogeneous grain batches of a specific quality grade. Wheat is easily attacked by pests or subjected to fermentation and sprouting if the correct moisture and temperature (both of the kernels and the environment) are not correctly maintained. Post-harvest losses of cereal grain may represent as much as 10% of the whole world production (Fleurat-Lessard 2004). Simple operations – such as turning and transferring grains from one bin to another while treating with dry air (aeration process) – are not expensive but are quite effective in controlling the moisture and temperature of the mass. These operations redistribute the temperature and moisture to make it uniform, thus avoiding spontaneous heating phenomena (Posner and Hibbs 1997).

Nowadays, as well as conventional fumigation processes (regulated by the legislation of each country but not allowed for organic wheat), physical treatments are becoming increasingly preferred as they give similar control of infestants without leaving chemical residues in the grains (Fields and White 2002). Both high- and low-temperature treatments protect grains from pests, although low temperatures are preferable. Values below 10 °C induce no modifications and/or interactions in functional macromolecules but inhibit activity of insects and fungi (Bailey 1992). Heating above 40 °C kills insects and promotes grain drying, but it can also induce internal fissuring and partial protein denaturation (Pomeranz 1992). Another alternative storage practice is the replacement of air with CO_2 or N_2, or their mixtures, to create a controlled atmosphere with a low oxygen content (less than 1.5%), appropriate for controlling pest development (Bell and Armitage 1992).

Grain cleaning

The wheat that arrives at the mill is usually transported in bulk in trucks, trains or ships and is unloaded into large hoppers with a grilled opening to facilitate the elimination of large foreign matter. This operation is preceded by rapid analytical inspections of representative samples of the entire batch to assess compliance with the quality parameters established by the company. Preliminary cleaning operations made before loading the wheat into the silos of the mill mainly remove coarse foreign matter and extend storage.

The actual cleaning of the wheat is made immediately before the milling process in the "cleaning house". Differences in the number and types of cleaning steps can be observed in the diagram used by each mill. In any case, some operations are essential. The cleaning system, therefore, involves a sequence of operations, each performed by a special machine with the aim of removing impurities, foreign materials, and powders. Difference in size, shape, density, kernel hardness and friability, and composition with respect to the whole and sound wheat grains is used to achieve this (Posner and Hibbs 1997; Posner 2009). Cleaning is often carried out in two stages, separated by a conditioning step. The second phase consists of a friction action carried out by a scourer to remove the outer pericarp layers, thus promoting a polishing effect.

Grain conditioning or tempering

The conditioning or tempering stage of the kernels is decisive for obtaining a good milling result. This operation covers both the grain humidification (using a tempering mixer) and the successive rest period so that a 2−4% increase in water content is reached. This conditioning reduces the friability of the bran, which causes it to break off as large particles, and mellows and makes the starchy endosperm more fragile, thereby facilitating separation between the two regions. The conditioning time (which varies between 6 and more than 24−36 h) and the quantity of water used – and the way it is added (1 or 2 tempering steps) – depend not only on the initial humidity of the material, but above all on the degree of hardness and vitreousness of the kernels. These parameters relate to the compactness with which the starch and proteins are organized in the endosperm (Chasseray 1991). After a rest period in the tempering bins, the caryopses have between 15.5 and 17% humidity, which is the best condition for milling (Posner and Hibbs 1997).

The milling process

The milling process involves complex types, numbers, and combinations of operations (Figure 2.5). It is generally classified into three systems: (1) the break system, which separates the endosperm from the bran and the germ; (2) the sizing and purification system, which separates and classifies particles according to the presence of bran pieces; (3) the reduction system, where the large particles of endosperm are reduced to flour (Lucisano and Pagani 1997).
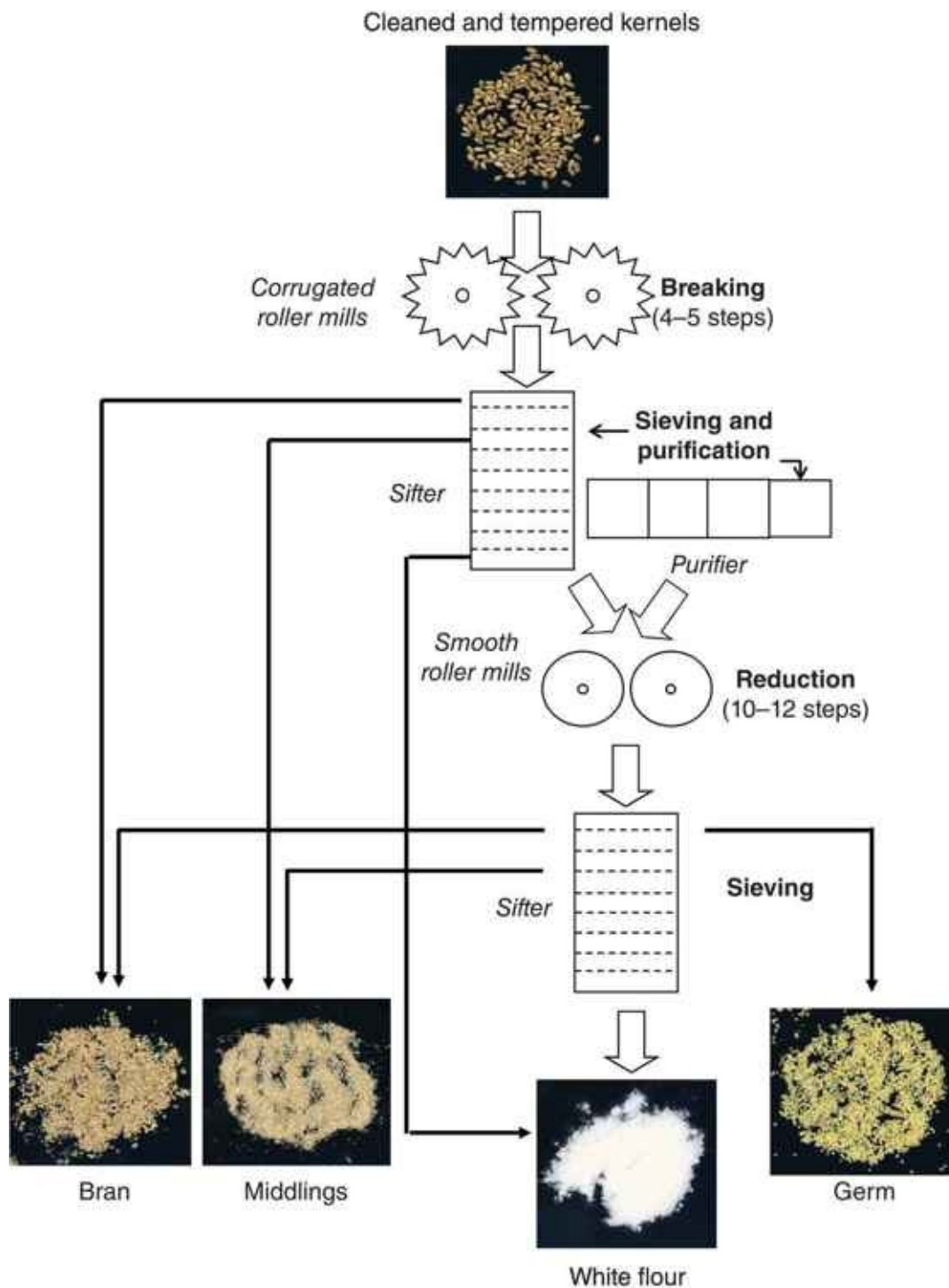
Figure 2.5 Simplified diagram of wheat milling operations.

The wheat grain has its first breaking in the roller mills, which are made up of a pair of cast iron chill cylinders with corrugated surfaces that are at a set distance from each other and turning at differential speeds towards each other ([Figure 2.6]). The breaking system has opens, cuts, and flakes the grains; separates the endosperm from the coats; and leaves the bran as large, flat flakes that facilitate its removal. As mentioned earlier, to do this, the grain must be ground gradually (generally 4–5 subsequent breaking steps are carried out), thus limiting the formation of flour and the disintegration of bran at this stage of the diagram (Webb and Owens 2003).

(a)

(b)
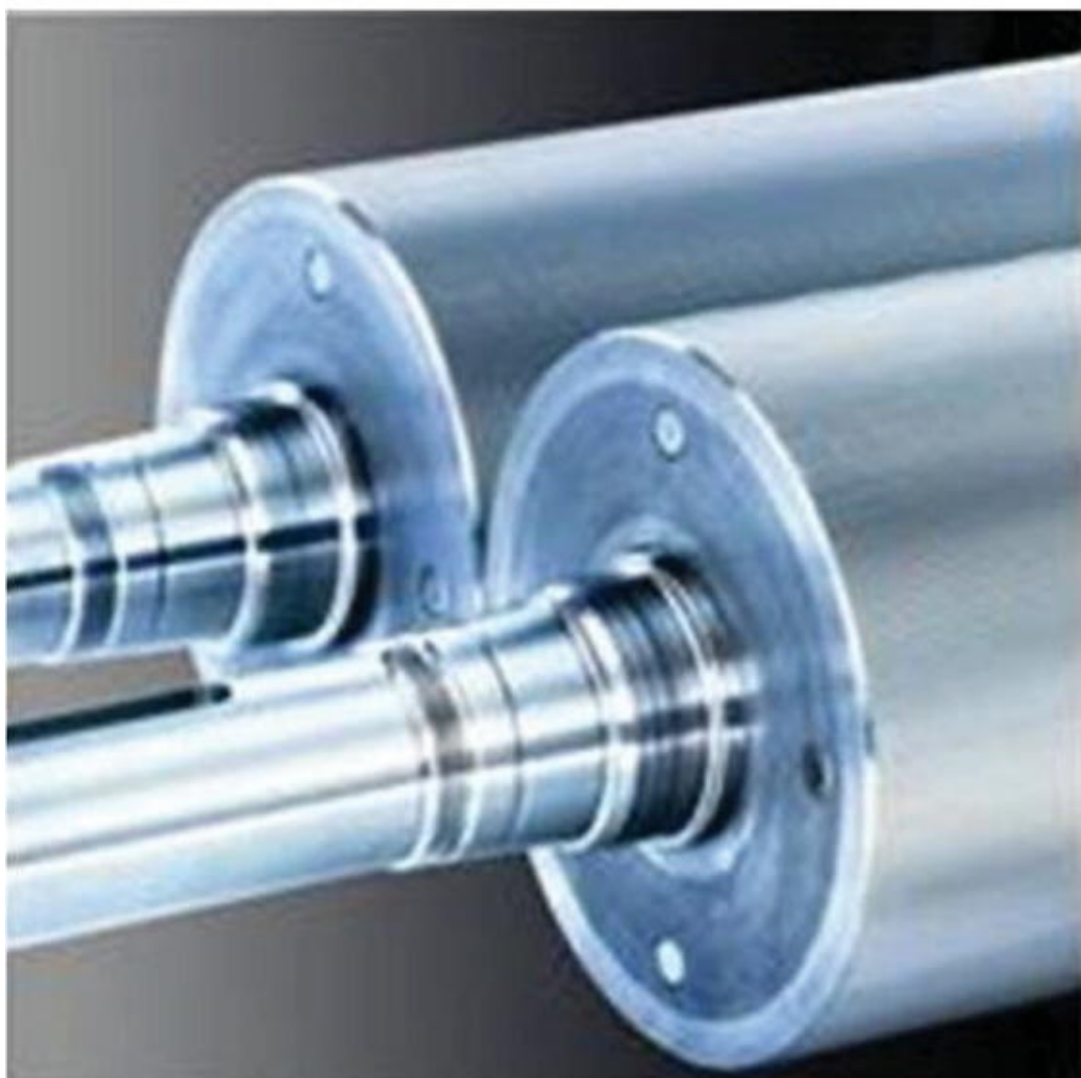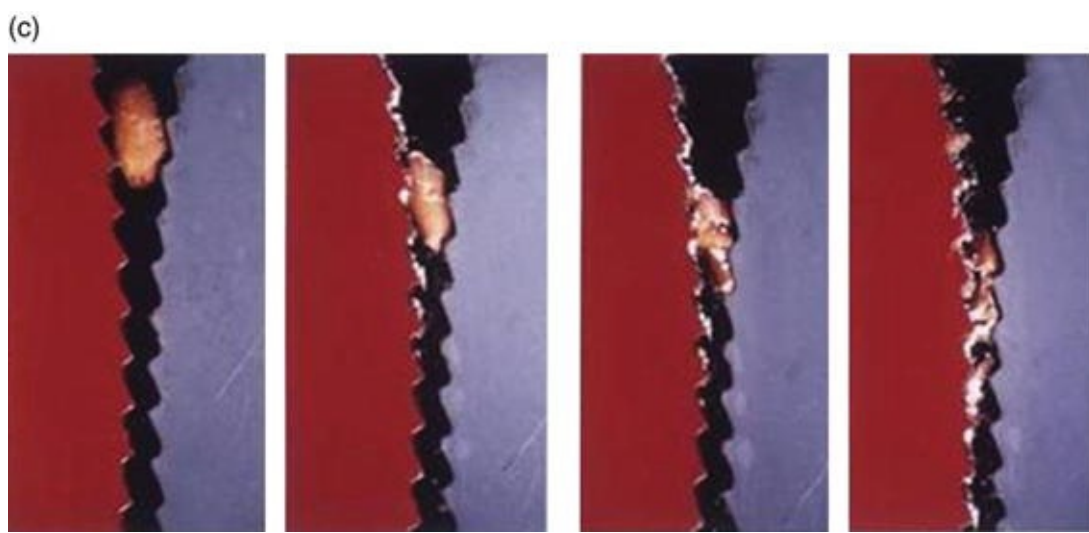
Figure 2.6 Break system: (a) roller mills (b) detail of corrugated rolls (c) progressive breaking effects on wheat kernel due to corrugated surface and differential roll speed (copyright and courtesy of Bühler Group).

Each breaking step is followed by sieving performed by plansichters or sifters, which are large machines stacked inside with numerous sieves of appropriate mesh (Figure 2.7). The coarse particles of endosperm are called "semolina". Some particles or "middlings" have various degrees of attached bran layers, whereas others – "clean middlings"– are composed of pure endosperm. These two fractions are separated using their specific gravity and the size inside the purifiers through which an air current passes upwards (Figure 2.8). The sizing rolls, formed by smooth or slightly corrugated rolls, detach the bran pieces attached to the middlings.

A = inlet
B = break
C = coarse middlings
D = medium middlings
E = fine middlings
F = coarse flour
G = flour
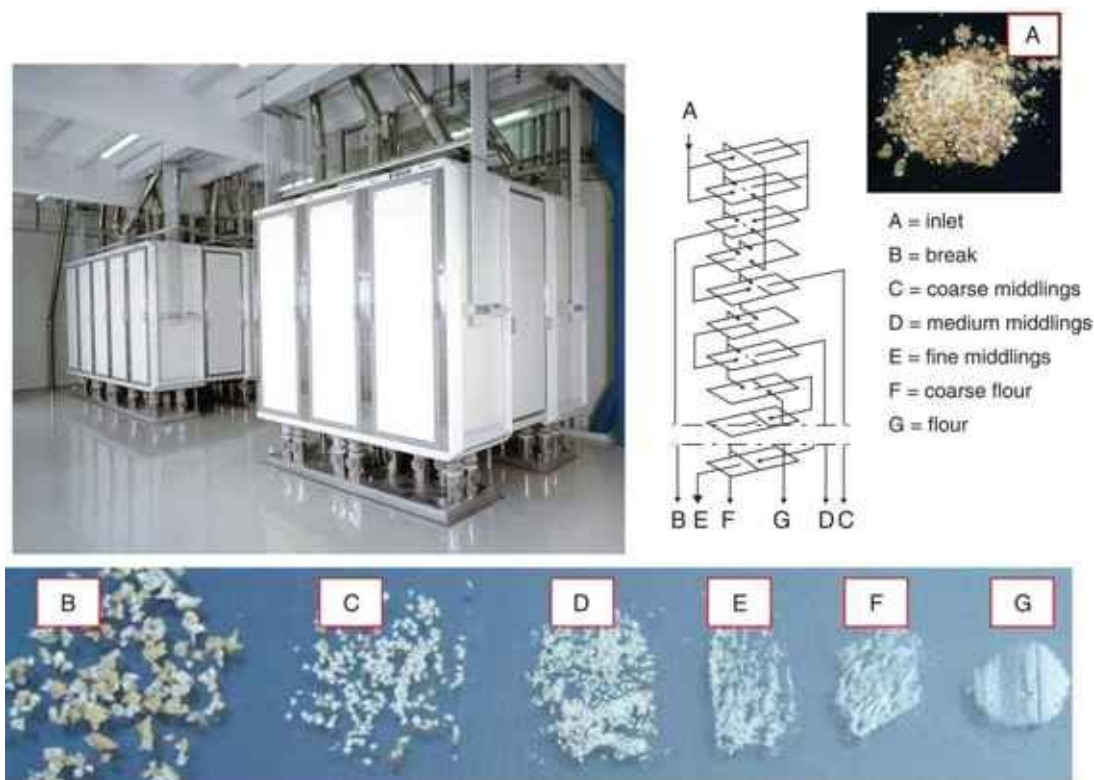
Figure 2.7 Sieving section: sifter or plansichters (top left) and diagram of the classification action (top right). The middling fractions separated by sieving action are shown in the bottom (copyright and courtesy of Bühler Group).

1) Inlet 2) Aspiration 3) Semolina (clean)
4) Semolina (composite) 5) Tailings
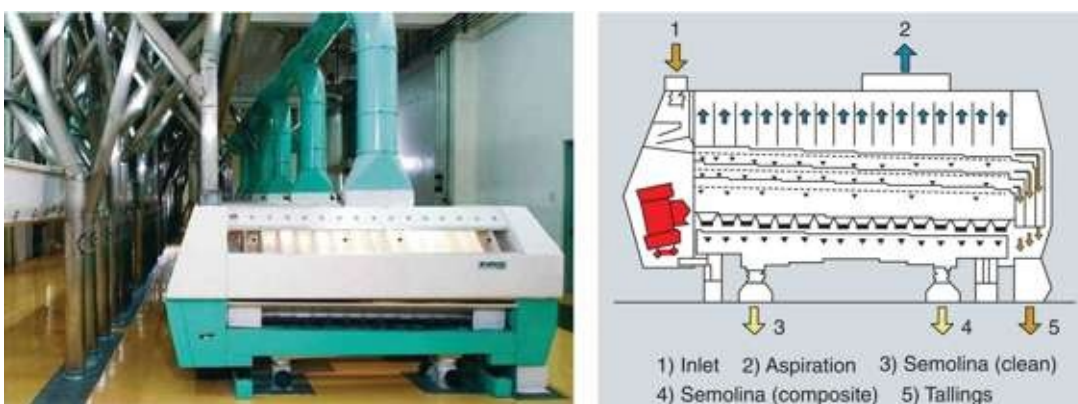
Figure 2.8 Purification system: purifier (left) and detail of cross-section (right) (copyright and courtesy of Bühler Group).

These operations are immediately followed by classification by the plansichters. The clean middlings are sent to the reduction system, the final stage in the milling process, which reduces the size of the clean middlings to flour. The reduction system consists of a sequence of several smooth roll mills (up to 8–12 according to the size and starch expected damage) and associated sifters.

The milling diagram comprises a number of these steps (varying from company to company according to specific requirements), finalized at ensuring that the majority of the endosperm is converted into flour, and that most of the coats are separated and removed as by-products. Summarizing, from each sieving step, an individual flour stream is separated; according to the milling passage, these intermediate streams are heterogeneous both in quantity and chemical composition. The careful blending of the intermediate streams gives an end-flour with the required refinement standards and chemical and rheological characteristics (Posner 2009).

Flour characteristics

Due to the high number of wheat varieties grown all around the world and the technological innovations in milling operations, the range of flours available nowadays is wider than ever before. This makes a skilful miller able to satisfy any customer's requirement and demand.

Milling yield and flour refinement

It is, however, possible to classify flour types according to a number of criteria. The first, the *milling yield* percentage, assumes both an economic and technological importance. It is expressed as number of kilograms of flour obtained from 100 kg of cleaned and conditioned wheat grains, and generally ranges between 74 and 76% for flour from common wheat. Since the bran and germ represent approximately 20% of the weight of the wheat grain, the actual yield in flour is distinctly lower than its theoretical value. The more refined the flour, the lower the extraction rate because during production the most external layers of the endosperm (namely the "fine middlings") are eliminated together with the teguments. The milling of durum wheat requires different diagrams, characterized by a higher number of purifiers to improve the separation of bran particles. Nevertheless, the yield is lower, between 68 and 72%, as semolina is mostly formed by particles larger than 250–300 μm and contains only a minimum amount of fine particles (less than 200 μm).

A widespread flour classification criterion is based on the accuracy of the separation of the bran, known as *flour refinement*. This index is closely related to the milling yield and influences flour color. Several intrinsic parameters of wheat kernel (such as hardness, test weight, moisture, ash and fiber content) and processing variables (such as mill diagram, setting of breaking rolls) greatly affect how the removal of branny layers is achieved. Classifying flour according to its refinement is regulated by the legislation of a various countries in which the milling yield of flour must comply to the threshold value of a number of parameters, particularly the ash and protein contents (Table 2.3), which are sensitive markers of the presence of bran.

Table 2.3 Flour classification in different countries according to the flour extraction rate and refinement level

Country	Denomination	Extraction rate (g/100 g dry kernel)	Ash (g/100 g dm)
USA	patent (45)	45	0.35 max
	patent (60)	60	0.37 max
	straight-grade/all purpose	74	0.40−0.50
	first class	~ 95	~ 1
France	45	65−70	< 0.50
	55	70−78	0.50−0.60
	65	74- 82	0.62−0.75
	80	80−85	0.75−0.90
	110	85- 90	1.00−1.20
	whole	90−98	> 1.40
Italy	00	70	0.55 max
	0	75	0.65 max
	1	80	0.80 max
	2	85	0.95 max
	whole	98	1.3−1.7
Germany	405	< 55	0.38−0.47
	550	70 max	0.49−0.58
	630	75 max	0.60−0.70
	812	80 max	0.75−0.87
	1050	85 max	1.00−1.15
	1200	90 max	1.16−1.35
	whole	> 90	1.8−2.0

Thus, it is possible to distinguish three basic flour categories from extraction rate and refinement properties:

- White flour: usually corresponding to 75% of the whole wheat grain. Most of the bran and wheat germ have been removed during milling.

- Wholemeal or Graham flour: 100% extraction yield, made from the whole wheat grain with nothing added or taken away. As stated by AACC (1999), "…the principal anatomical components – the starchy endosperm, germ and bran – are present in the same relative proportions as they exist in the intact caryopsis".

- Brown flour: usually contains about 85% of the original grain, some bran and germ have been removed to extend shelf-life.

Sometimes, highly refined flours are produced for particular purposes, such as the flour for

fresh pasta production (Pagani and others 2007) in which the low extraction rate (about 30%) assures the accurate removal of the enzymes present in the germ, bran, and peripheral endosperm regions. Consequently, fresh pasta keeps its characteristic white color, highly appreciated by consumers, without the development of graying. The opposite situation characterizes high extraction rate flours: the high content of fibers, enzymes, and lipids causes a definite worsening of the rheological and technological behavior of the flour. Note that high degrees of extraction are inevitably associated with lower flour preservability due to rancidity phenomena.

Technological properties of flour

Although the evaluation of the refinement degree is an important criterion in the classification of flours, it is not sufficient for completing the description of their suitability for a specific end-use and for predicting their behavior during an artisan or industrial technological cycle. The baker asks the miller for information on the ability of the flour to absorb high quantities of water and to form dough that can develop without collapsing either during the leavening or the baking phases.

Certainly, the protein content is linked to the compactness of the gluten network. Nevertheless, the miller completes the definition of the characteristics of the flours with numerous *rheological indices*, aimed at predicting behavior in a real transformation process. Even though starch is arguably the most important component in any flour, it is universally held that the protein – and gluten in particular – is responsible for the functional quality of the product. It follows that the majority of rheological tests made until now have examined the *viscoelastic behavior* of the gluten fraction under physical, mechanical, and thermal stress, similar in nature and intensity to those that occur during a real mixing and leavening processes. Conventionally, and independently of the extraction rate, it is usual to subdivide flours into strong, medium, and weak flours, according to their end-use (Lafiandra and D'Egidio 2010). The standards adopted by the Italian market are summarized in Table 2.4.

Table 2.4 Flour classification according to chemical and technological parameters (adapted from Cocchi and others 2005)

Wheat grade	Protein N * 5.70 (g/100 g dm)	Alveographic indices		Farinographic stability (min)
		W $(J * 10^{-4})$	P/L	
Improver wheat (FF) (very strong gluten)	> 14.5	> 300	< 1	> 15
Superior bread-making wheat (FPS)	12.5–14.5	220–300	< 0.7	10–15
Ordinary bread-making wheat (FP)	10.5–12.5	160–200	< 0.6	5–10
Wheat for biscuits (FB) (weak gluten)	< 10.5	< 115	< 0.5	Not determined

The role of starch has only recently been investigated, particularly the fraction called damaged starch, which originates during the milling stage in different quantities according to

the characteristics of the kernel and the milling conditions. This fraction is more susceptible to amylolytic enzyme action than undamaged starch and exhibits a higher degree of water absorption (Mok and Dick 1991). In soft wheat products, especially cookies, high levels of damaged starch are detrimental to quality (Gaines and others 1988). For hard wheat products, such as bread, damaged starch levels should be favorable for leavening, in particular in formulas containing little or no added sugar. However, high levels of damaged starch negatively affect the dough rheology, causing handling problems (Bushuk and Scanlon 1993) and worsening baking performance (Cauvain and Young 2006; Barrera and others 2007).

Nutritional properties of flour

The separation of the germ and the bran (regions rich in several bioactive and functional compounds) during the milling process inevitably produces a profound change in the chemical composition and consequently in the nutritional value of the finished product. In particular, flour has a lower concentration of ashes, proteins, vitamins, and soluble sugars than the caryopsis, and a greater starch content. The relative difference between the composition of the grain and that of the finished products obviously depends on the efficiency of the separation of bran layers from the endosperm. Consequently, a refined flour with an extraction rate of approximately 75% contains only 5% fiber, and – with respect to the original caryopsis – 45% fats, 30% minerals and between 15% and 40% different vitamins. On the other hand, the starch content is higher by 10% in flour ([Figure 2.9](#)).
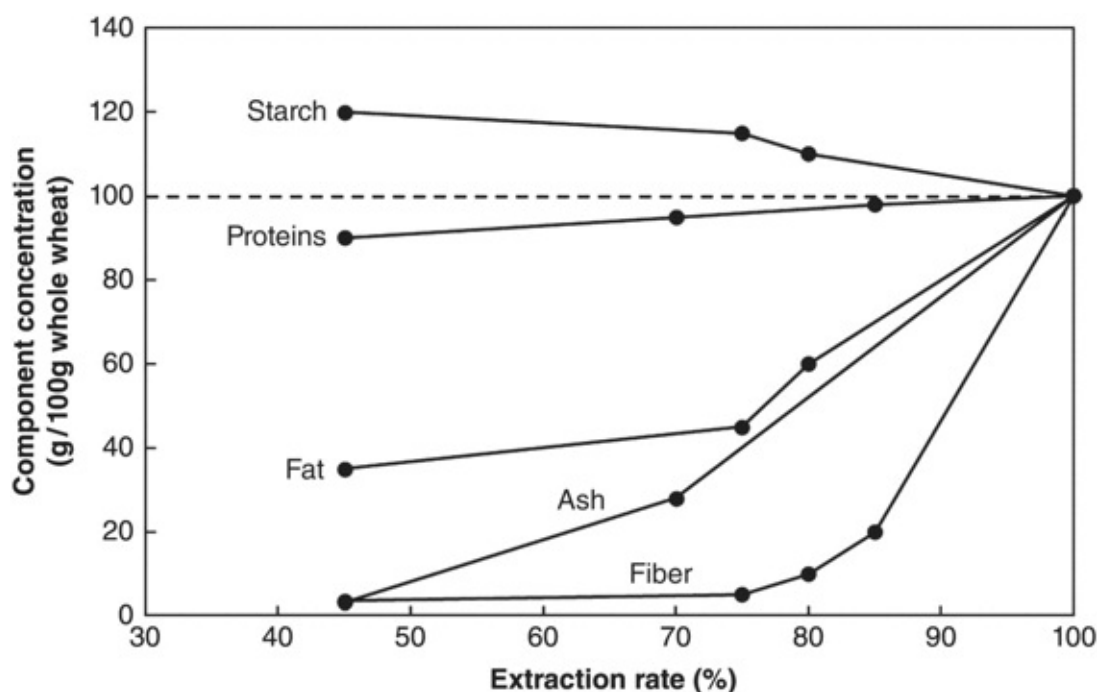
Figure 2.9 Composition of flour according to the extraction rate: comparison with whole kernel (dotted line) (adapted from Lucisano and Pagani 1997).

To improve the nutritional and functional characteristics of flour, under the 6th Framework Food Research Program, the European Community supported the huge Integrated Project HEALTHGRAIN on whole grain cereals and cereal products (www.healthgrain.eu). The project, which ended in 2010, intended to "provide a scientific basis for a new generation of healthy cereal-based products – beyond whole grain". One of the final documents of the HEALTHGRAIN Project (Delcour and others 2012) gathers and examines the new processing

technologies set up by several research groups during the project, giving interesting indications about new milling processes.

Optimization and innovation in wheat milling

At the end of the last century, there was a significant inversion of trends in wheat milling. In the 1980s and 1990s, the main objective of this sector was process cost reduction. The easiest solutions were those that guaranteed high flour yields with the lowest number of roll mills, sieving machines, or purifier machines.

In the past decade, new food safety-related regulations – for example, Hazard Analysis and Critical Control Point, traceability, labeling health claims, and use of genetically modified organisms (FAO/WHO 1997) – have supported an improvement in process control in the milling and bakery industries (Werner 2002; Sperber, 2007). Moreover, the intense competition between companies, the new international laws on food safety and traceability (ISO 2005, Standard 22000; ISO 2007, Standard 22005; ISO 2008, Standard 9001), and increased consumer discernment have shifted attention towards technological solutions that not only consider the production and economic aspects of the process, but also the quality characteristics of the flour. In particular, the hygienic, nutritional, and functional (high content of biocompounds, soluble fiber, resistant starch) aspects are monitored as well as the technological performance required by the bakery industry.

Grain storage

Ozone (O_3) has found use as a fumigant in controlling stored-grain insect pests and microorganisms (Fiwari and others 2010; McDonough and others 2011). Mendez and others (2003) investigated the effects of ozone exposure on the end-use properties of different cereals and pulses. Laboratory-scale treatments at 50 ppm for 30 days did not produce any detrimental effects either on the milling characteristics of the wheat or on the baking properties of the corresponding flour, maintaining the fatty acid and amino acid composition. Another recent study showed positive results in a commercial steel grain bin filled with 13.6 tonnes of hard red winter wheat (Hardin and others 2010).

Grain cleaning

In most of the milling diagrams, the grain cleaning operations are performed using a significant number of machines until all the so-called foreign matter of different origin, size, and composition is removed.

The most recent innovation proposed for this stage is the substitution of these machines with an optical sorter (www.buhlergroup.com), a device which efficiently removes all types of contaminants and foreign materials in a single step and which until now has only been used in rice processing. The product stream is fed into the sorting machine and different high-resolution cameras detect and recognize defects on the basis of color, shape, and other optical properties. Specific sensors and high-speed ejectors carry out a precise ejection, enabling high-speed and accurate separation of contaminants (Figure 2.10).

Figure 2.10 The optical sorter (Sortex) (left) and examples of the impurities removed (right) (copyright and courtesy of Bühler Group).

Debranning and pearling processes

Debranning technology (also reported as preprocessing or pearling) has become well established in rice milling and barley processing for removing hulls that have no technological and/or nutritional interest (Dexter and Wood 1996). Although this practice is necessary for covered cereals, the sequential removal of the outer kernel bran layers prior to milling has been quite uncommon in "naked" grain processing.

Since the 1960s, several studies on the debranning of durum wheat (*Triticum durum* sp.) have been carried out at the laboratory scale, suggesting that this premilling operation is a useful tool for increasing yield while lowering the ash content of semolina (Grosh and others 1960; Pomeranz 1961). The first interesting results date to the 1990s, when the machines used for covered cereals were modified for pearling wheat kernels (Tkac 1992; Wellman 1992; McGee 1995).

The oldest debranning systems for wheat are the Tkac process and the PeriTec process marketed by Satake Corporation (www.satake-group.com). The heart of the Tkac system is represented by two horizontal processing machines: the first one strips out the outer bran layers by friction (kernel to kernel); a second one removes most of the seed coats, some of the nucellar tissue and the aleurone cells by abrasion (kernel to stone surface) (Tkac 1992). The PeriTec procedure also uses two different machines, but with a vertical configuration (Dexter and Wood 1996; Willis and Giles 2001). In both processes, durum wheat kernels are conditioned with water and processed after a few minutes; these conditions assure water penetrates only into the outermost regions of the seed coat. New debranning equipment for wheat has been developed to carry out abrasion and friction in the same machine. The Vertical Debranner VCW (Satake Corporation) includes two separate working chambers in the same equipment. The upper chamber has an abrasive zone where rotating abrasive rings work the grain against a peripheral slotted screen through which the outer bran layers are drawn. Partially debranned grains then enter the lower chamber, where friction completes the debranning process.

Due to the positive results obtained with durum wheat by several research groups worldwide (Dexter and others 1994), attention shifted to common wheat (*Triticum aestivum*). However, the advantages obtained until now for this cereal are limited and contradictory. Applying the

Tkac system to several common wheat varieties, Dexter and others (1994) found inconsistent milling advantages. However, others highlighted the decrease in microbial contamination (Laca and others 2006) and bunt infections (Sekhon and others 1992). Pearling of common wheat was also tested on sprouted wheat kernels for reducing their α-amylase activity, making them suitable for baking processes (Henry and others 1986; Liu and others 1986; Hareland 2003). These positive results were generally obtained using a laboratory-scale machine. Bottega and others (2009) evaluated the effects of different debranning conditions on several characteristics of common wheat kernels by using a pilot plant equipped with innovative abrasive rolls covered with synthetic diamond powder. The effects of the abrasive action seemed highly influenced by the grain pretreatment conditions. The best result was obtained with a debranning level of 10–12% and a short prehydration step. Moreover, a brushing passage performed by a conventional scourer machine was necessary to eliminate some bran particles raised by the mechanical action and still present on the kernel surface after debranning (Figure 2.11).

(a)

(b)

(c)

(d)

1mm

EHT = 20.00 kV

Detector = SE1

Date :19 Jun 2006

(e)

100µm

EHT = 20.00 kV

Detector = SE1

Date :26 Jan 2006
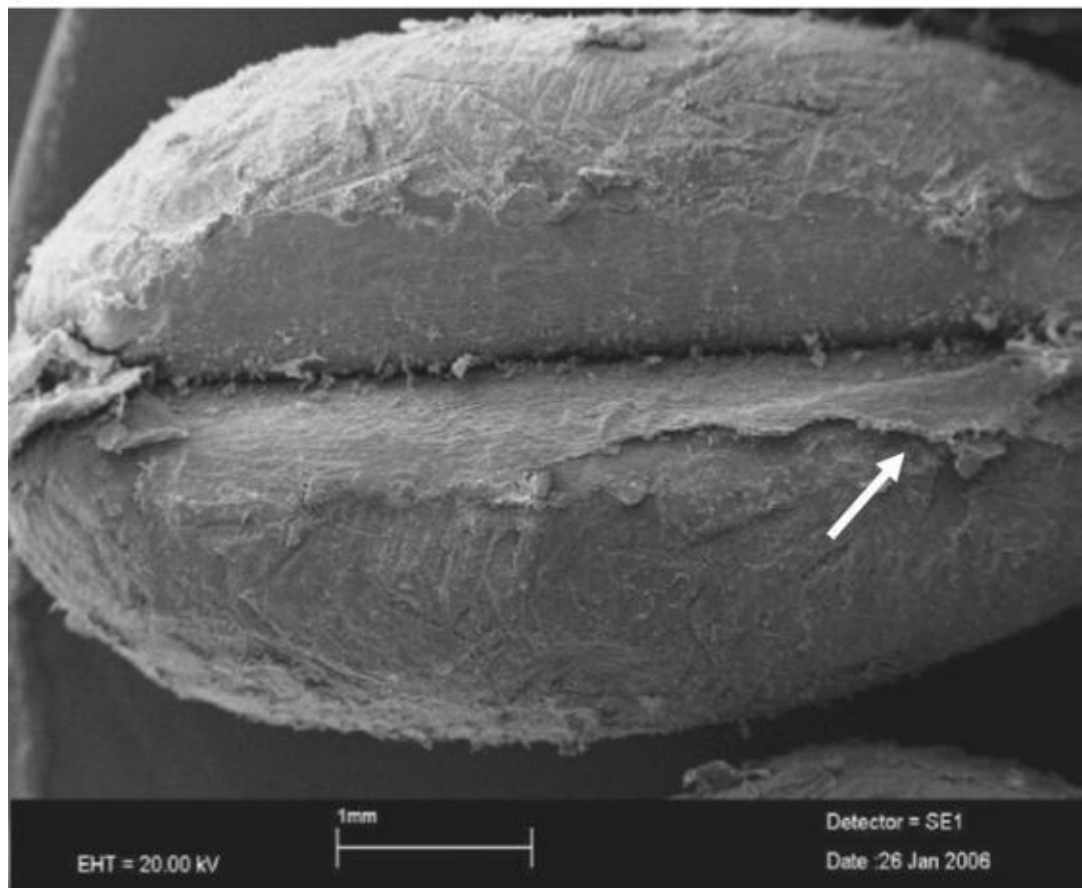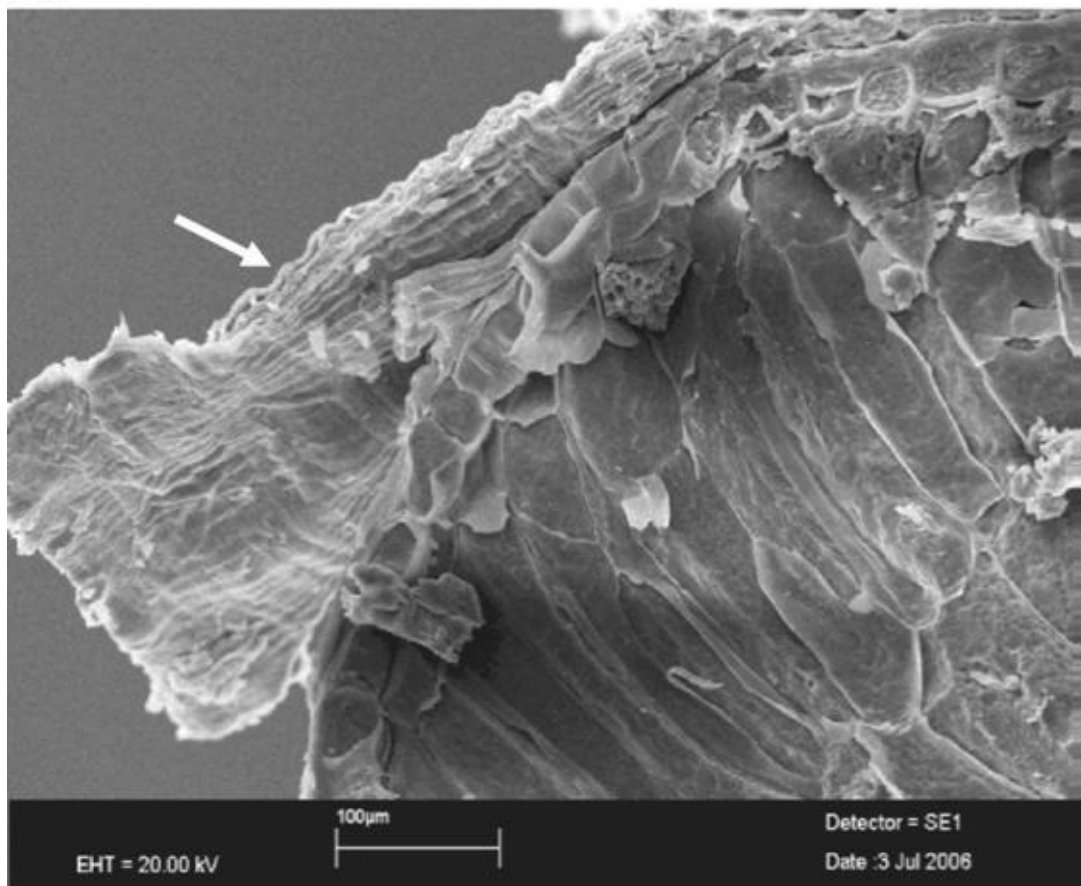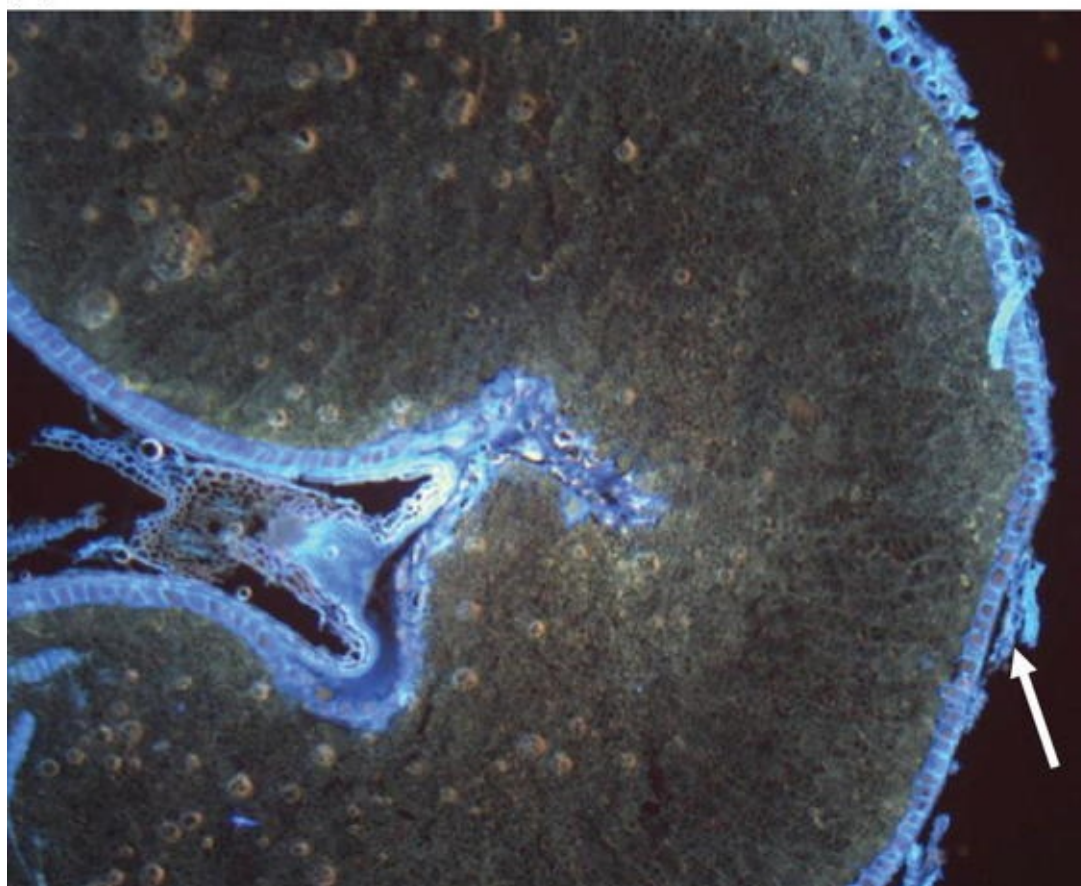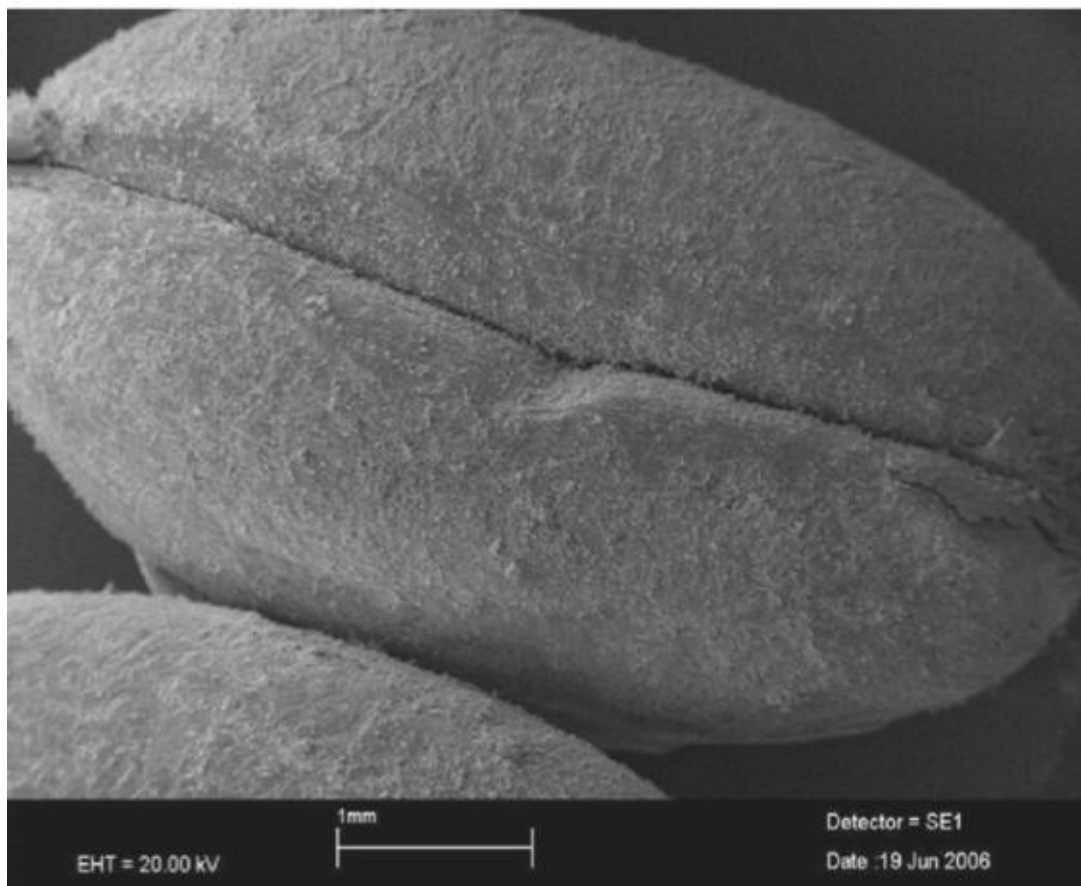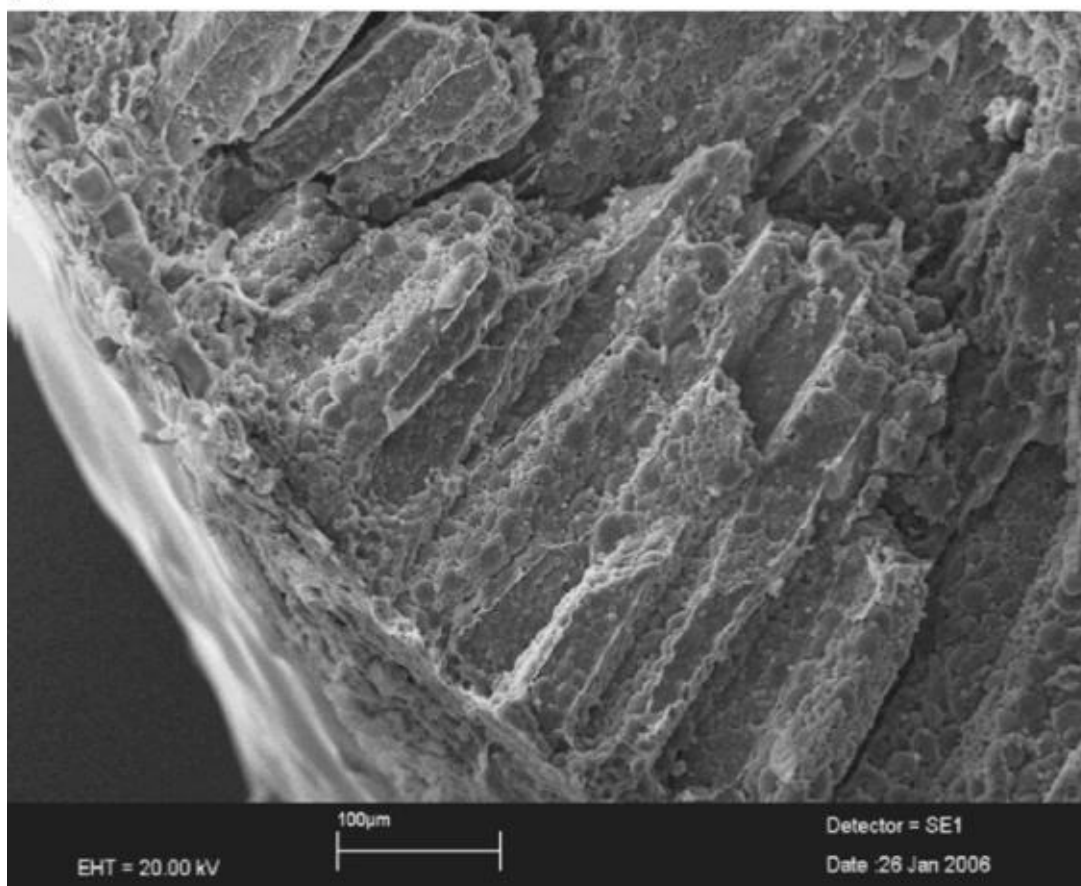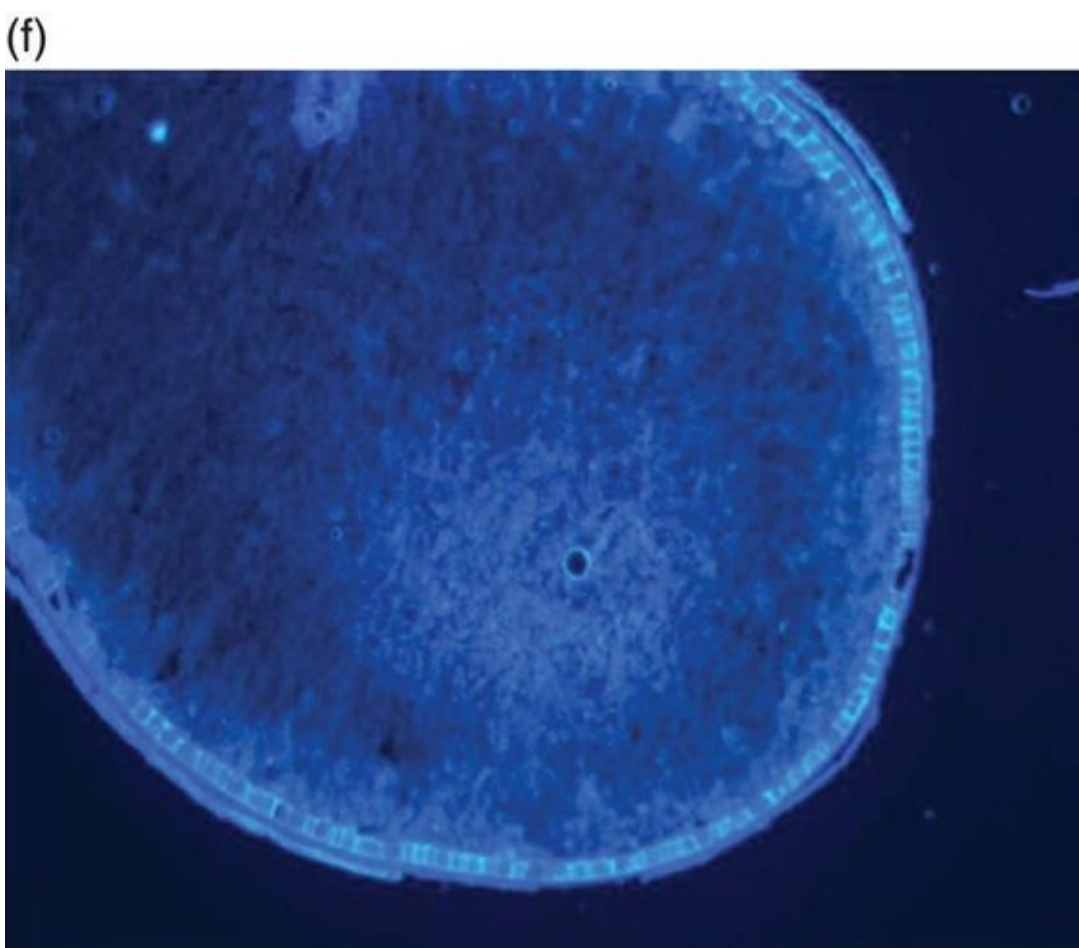
Figure 2.11 Images of debranned hard wheat kernels before (a, b, and c) and after brushing passage (d, e, and f). Arrows show the bran layers still present in the crease area (a), and raised by debranning action (b and c). The brushing passage completes the removal of bran layers, giving a smooth surface (d, e, and f). Scanning electron microscopy (a, b, d, and e) and fluorescence microscopy (c and f) images.

Taking all this into consideration, at present the industrial premilling treatment of common wheat consists of a peeling process carried out with a machine (such as the DC-Peeler recently proposed by Bühler AG, www.buhlergroup.com; or the DHA Vertical Debranner from Ocrim S.p.A., www.ocrim.it) which promotes a mild removal of the outermost layer of kernel (maximum 1.5–2 % of the grain weight) and, at the same time makes it possible to reduce contamination by 50%.

Improvement of flour performance and exploitation of ancient milling processes

As mentioned earlier, wheat is the only cereal that can be transformed into an extremely wide range of products. This natural capacity has been further improved by selective breeding research aimed at obtaining varieties able to better satisfy the requirements for the final use of the flour. These programs mainly concern both quality and quantity changes in the seed storage proteins. Nonetheless, the real performance of wheat during the technological process is often different from expectations since the characteristics of the raw material are strongly influenced by environmental and agronomic parameters (Wrigley and Batey 2003; Carson and Edwards 2009). The practice of improving the working capacity (technological functionality) of the flours with the addition of improvers is therefore significantly

widespread. Among the most commonly used improvers are enzymes (such as amylase, hemicellulase, lipase, protease) and emulsifiers (such as monoglycerides and diglycerides), that can increase the dough development, gas retention, and crumb softness both in fresh bread and during storage. Note that many of these improvers are already naturally present in the wheat grain but are removed with the by-products (bran and germ) during milling as they are located mostly in the external peripheral areas. These, as mentioned earlier, are responsible for significant deterioration of both the rheological and the hygienic characteristics of the dough, as well as turning it rancid quickly.

Recently, an Italian milling company (www.molinoquaglia.com) designed a particular milling process that uses millstones to obtains a less refined flour (called "Petra flour"), which is richer in the external peripheral areas compared to refined flour obtained from the same grain. The process involves a preliminary peeling of the caryopses to lower natural contamination after a shorter humidification period than that used in conventional milling processes (this is important for ensuring that the grain is ground to give a bran of the correct granulometry). Then the grain is stone milled, recovering only the granulometric fraction lower than 200 μm. This material collects both part of the endosperm and some bran layers, rich not only in minerals but also in enzymatic proteins, polar lipids with emulsifying properties, and fiber, especially soluble fiber (Table 2.5). The positive effect in bread making is also clearly shown in the Table 2.5; the greater quantity of fiber and minerals does not compromise the dough development capacity, and guarantees an alveolar structure that is similar to that of bread made with refined flour, but with greater nutritional characteristics.

Table 2.5 Comparison of chemical composition and rheological characteristics of "All purpose" flour and "Petra" flour. The corresponding bread aspect (sponge and dough process) is also shown

Parameter	All purpose flour	Petra flour[a]
Protein (g/100 g dm)	13.5–14.5	13.0–14.0
Gluten (g/100 g dm)	44.0–46.0	44.0–46.0
Fat (g/100 g dm)	0.8–1.2	1.2–1.4
Ash (g/100 g dm)	0.55–0.65	max 0.80
Dietary fiber (g/100 g dm)	3.0–3.5	6.7–7.0
Farinographic indices:		
Water absorption (%)	58.6	60
Dough stability (min)	19	14
Rheofermentographic indices:		
Dough development (mm)	62.5	61.2
CO_2 production (mm) mm	1553	1590
Retention coefficient (%)	91.4	90.6
Bread aspect		

[a]Courtesy of Molino Quaglia S.p.A.

Exploitation of milling by-products

Milling by-products are usually diverted to feed. They include wheat bran, wheat middlings, millrun, shorts, red dog, wheat germ meal, and high-purity germ (Posner 2009).

Wheat germ

Wheat germ, which represents 2.5–3.0% of the kernel, contains highly concentrated nutrients (Table 2.1). In addition, wheat germ is reported as one of the most excellent sources of the vitamins E and B group, dietary fiber, calories, and essential amino acids (Sjövall and others 2000; Ge and others 2000; Arrigoni and others 2002. It is also a good source of some functional phytochemicals as flavonoids, sterols, octacosanols, and glutathione (Zhu and others 1986). Its interesting nutritional composition and high palatability makes germ a raw material potentially suitable for the enrichment of bakery products. On the other hand, its poor storage stability, due to the large amount of unsaturated fats as well as to the presence of hydrolytic and oxidative enzymes, makes germ highly susceptible to rancidity, limiting its utilization (Srivastava and others 2007).

Several efforts have been made to stabilize and improve germ shelf-life. All approaches point at stopping enzyme activity, with particular attention to lipase and lipoxygenase. This can be achieved directly, using thermal treatments to eliminate enzyme activity, or indirectly, by creating adverse conditions for their action (for example, by acidification, oxygen elimination, and so on). Until the 1980s, heat treatments (toasting, hot air process, and pressure extrusion) were the only methods for slowing rancidity development (Haridas Rao and others 1980). More recently, extrusion cooking and microwave heating have resulted in rapid and efficacious enzyme inactivation (Matucci and others 2004).

Despite their effectiveness, heat treatments may be expensive, not resolutive, and negatively affect the nutritional value of the wheat germ. Recently, sourdough fermentation has been used for stabilizing and enhancing some nutritional properties of wheat germ (Rizzello and others 2010). Due to lactic acid fermentation, lipase activity of fermented wheat germ was 2.5-fold lower than that found in the raw germ. Moreover, this bioprocess increased the content of free amino acids, total phenols, phytase, and antioxidant activities. The effectiveness of sourdough fermentation was also confirmed by Bottega and others (2012). Fermentation, in fact, provided a sharp inactivation of several enzymatic activities, accounting for the low hexanal value after germ storage at 25 °C for 80 days. After storage, the amount of this volatile aldehyde, commonly taken as a sensitive marker of lipid oxidation and food rancidity, was five times higher in raw germ compared to the fermented and dried germ (Bottega and others 2012).

Wheat bran

Wheat bran (about 18–20% of the whole grain) includes all the external layers of kernels, such as pericarp, seed coats, nucellus, and aleurone cells (Antoine and others 2004). The presence of bran negatively affects the loaf volume due to several mechanisms (Finney and others 1985). Bran particles disrupt gluten continuity, preventing a regular 3D expansion of gas cells and favoring their elongation (Salmenkallio-Marttila and others 2001). The presence

of bran also greatly affects the hydration phenomena of flour (Shogren and others 1981; Moder and others 1984). Changes in the functional properties of flour vary with the particle size of the bran, but studies have led to contradictory results as both the physical properties (actual particle size range) and chemical composition should be taken into account. Bran may contain only the external coat layers or the aleurone as well (Lai and others 1989).

In 2001, Salmenkallio-Marttila and others proposed preprocessing the bran fraction by fermentation to improve the quality of bran-enriched bread. Positive effects in bread-making performances were also observed after enzymatic hydrolysis of bran (Marti and others 2014). The non-starch polysaccharides are broken down, favoring their solubilization and the maintenance of rheological performances. Other bioprocessing techniques, such as enzyme-aided fermentation, promoted similar results for fiber solubilization, and improved the bioaccessibility of phenolic acids with beneficial implications for anti-inflammatory properties (Anson and others 2009).

Assessing dough rheology for predicting baking performance

The actual technological behavior of flour is not only linked to the protein and gluten content, but it is also the result of complex interactions between macromolecules that are responsible for dough development. Consequently, flour classification is expressed by several parameters, usually measured by rheological approaches that generally provide a quantitative description of the mechanical properties as well as information related to the molecular structure and composition of the material (Dobraszczyk and Morgenstern 2003). Although the rheological properties of wheat have been investigated since the beginning of the 1900s, they still are considered of great importance for determining baking quality (Ktenioudaki and others 2010) and useful tools for predicting process efficiency (dough yield, leavening conditions, and so on) and product quality (such as specific volume, textural attributes) (Osborne and others 2007; Mondal and Datta 2008).

Wheat rheological properties can be measured using two main approaches: descriptive or empirical tests and fundamental measurements (Dobraszczyk and Morgenstern 2003). In this chapter, attention is given to empiric rheology, since it greatly reflects the behavior of raw material during processing and provides information on the quality of the final products. In fact, the basic principle of many empirical tests is to mimic each step of the baking process. Therefore, one possible criterion for classifying the tests is the processing step they simulate: mixing, proofing, or baking.

Prediction of mixing performance

During mixing, ingredients are distributed and blended within the mass. This phase is described as "dough development", a term which covers a number of complex physical and chemical changes responsible for the formation of gluten, a fascinating phenomenon which requires both the hydration of the proteins in the flour and the application of energy during kneading (Cauvain 2001). To assess the characteristics of the dough, the baker uses his hands and his acquired experience to judge the viscosity and elastic properties of the dough (Weipert 2006). Starting from this principle, several recording mixers have been developed to simulate mixing under laboratory conditions. The basic idea is to follow the formation of the dough. The torque developed by the mixer is measured and recorded throughout mixing. Many empirical tests can be used to predict water absorption by the dough, dough stiffness, and mixing requirements, including the flour's ability to support overmixing.

The most widely used recoding mixers are the *Farinograph* (www.brabender.com) and the *Mixograph* (www.national-mfg.com). These two instruments differ in the shape of the paddles and, consequently, in the mechanical stress to which the dough is exposed. Moreover, the dough is prepared with different amounts of flour and flour : water ratios (Weipert 2006).

The Farinograph by Brabender GmbH and Co. KG (Duisburg, Germany) consists of a dough-mixing chamber attached to a torque recorder. It measures the resistance of a dough against sigmoid-shaped mixing paddles turning at 63 rpm) (D'Appolonia and Kunerth 1984). The paddles hold a flour–water dough (constant flour weight: 300, 50, or 10 g of dry flour) to a

prolonged, relatively gentle kneading action, at a constant temperature (30 °C). The test (AACCI 2004, Method 54.21; ICC 2001, Standard 115/1) gives two important physical properties of flour: (1) the absorption or the amount of water required for the dough to reach a definite consistency; (2) a general profile of the mixing behavior of the dough (Locken and others 1991).

The first step of the test is the "titration phase". A standard weight of flour is placed in the mixing chamber and water is titrated from a buret into the flour to produce dough with an optimum consistency (500 Brabender Unit, BU). In the new Farinograph-AT, water is added to the flour by an automatic water dosing system, avoiding the influence of the operator in this critical step of the test. Different flours show differences in water absorption according to their quality. Despite the role of the flour, note that the "level of absorption" or "hydration" is greatly affected by the bread formulation (for example, the presence or absence of fibers, sugars, salt, fat, and so on) and the processing conditions. In some processes, the level of absorption does not correspond to the optimal quantity as determined by the Farinograph, but it is mainly related to the handling characteristics of the dough (Pagani and others 2010). Stiff doughs with hydration levels between 40–45% have reduced extensibility; consequently, the baked goods have a limited porosity with a very fine alveolar structure. In contrast, soft doughs have hydration levels higher than 60% and, consequently, they are difficult to handle due to their low consistency, which is responsible for the long and irregular shape and for the presence of large alveoli in the crumb that result from the coalescence of smaller bubbles (Pagani and others 2006).

There are two main parameters for the mixing behavior of the dough calculated from each farinogram. (1) Development time, corresponding to the time in minutes required for the dough to reach a point of maximal dough consistency before any indication of dough breakdown. It provides a measure of dough strength. (2) Stability or tolerance time, corresponding to the time in minutes during which the farinogram shades the 500 BU. It provides a measure of the mixing tolerance of the dough and is also related to the dough strength. A strong wheat flour takes longer to develop before reaching 500 BU, where it remains for some time at good stability and shows only a minor decline in consistency. A weak wheat flour reaches 500 BU quickly and undergoes a considerable decline in consistency showing little or no stability. Starting from the information about the development time and the stability, it is possible to define how much energy input a flour needs to produce good quality bread and to avoid the overmixing phenomenon (Weipert 2006).

The Mixograph is mainly a tool for plant breeders, as it requires very small sample amounts (2, 10, and 35 g), and contributes to the evaluation of the baking quality of the seeds under selection. The Mixograph test (AACCI 2004, Method 54–40.02) is used more in the United States than in European countries and, measures the resistance of a dough to mixing with pins. The dough is subjected to a rotating motion and to stretching so that it is squeezed and folded, and consequently, it is subjected to greater mechanical stresses than dough mixed in a Farinograph mixer (Weipert 2006). Moreover, the Mixograph always operates with a constant amount of water which results in dough of different consistency (Weipert 1990; Mann and others 2008). The recorded response gives the following indices: (1) peak time, corresponding to the dough development time; (2) peak height, a measure of the dough resistance to the extension caused by the passage of the pins; (3) mixing tolerance, corresponding to the resistance of the dough to breakdown during continued mixing (Vergnes

and others 2003).

More recently, *DoughLAB* (www.perten.com) and *Mixolab* (www.chopin.fr) – see next section – were introduced. Both pieces of equipment yield similar traces to those obtained with the Farinograph and Mixograph.

Prediction of proofing performance

Proofing (or leavening) can be considered the key step in bread making. The CO_2 from the yeast diffuses into the air bubbles incorporated in the dough during mixing, leading to the formation of an aerated crumb structure whose appearance greatly contributes to the sensory assessment and consumer acceptability of bread (Dobraszczyk and others 2000; Heenan and others 2008; Lassoued and others 2008). Gas production is highly affected by the amount of yeast and the fermentation conditions, whereas gas retention is related to the development and rheological properties of the dough (Cauvain 2009).

The behavior of the dough during fermentation can be shown and described using the *Rheofermentometer* (www.chopin.fr). It provides a complete overview of the macroscopic changes in the dough during fermentation as it measures the production and retention of CO_2 and the volume increase of the dough in a single test. These parameters are measured in real time (3 h), during which two curves are simultaneously generated: the first curve describes the so-called "dough development", whereas the second quantifies the volume of total CO_2 produced by the yeast, as well as the volume of CO_2 released from the dough and the relative time courses.

Dough resistance to mechanical stress can be also predicted and described using the *Alveograph* (www.chopin.fr) and the *Extensograph* (www.brabender.com). In these tests, the dough is subjected to intensive deformation until it breaks. The resistance curve of the dough during stretching is recorded and two main parameters are determined: resistance to large deformations, and stretching suitability. The Alveograph and the Extensograph provide deformations similar to those that take place during fermentation and oven-rise, with higher rates of deformation (Vergnes and others 2003). These tests measure the stress–strain relationships in the dough after defined rest periods (Faridi and Rasper 1987; Rasper and Preston 1991) so that the dough extension characteristics useful for predicting bread-making quality and for evaluating the specific effects of dough ingredients and additives can be determined (Bloksma 1990a, 1990b; Kokelaar and others 1996).

The Alveograph (ICC Standard 121 2001) is specifically designed to measure resistance to a 3D extension of a thin sheet of dough, prepared at a constant hydration level (43.3%) (Faridi and Rasper 1987), and simulating the sheeting, rounding, and molding of the baking process. Dough is shaped into disks and allowed to relax for 20 min. After that, air is blown under each disk, thus creating a bubble; the pressure inside the bubble is recorded until rupture occurs, giving the dough resistance to expansion and extensibility. Measurements made on the average curve for the five replicates include: peak height (P, mm), related to dough tenacity; curve length (L, mm), related to dough extensibility; work input (W, J), which is the amount of work required for the deformation of the dough and is related to the baking "strength" of the flour. Damaged starch and fiber content will considerably affect the response when working at a constant hydration level. Consequently, Chopin Technologies (Villeneuve-la-Garenne Cedex, France) proposed the *Alveo-consistograph* for the

determination of resistance of deformation, dough extensibility, and mixing energy of a dough prepared at a given consistency (AACCI 2004, Method 54–50), in conditions more similar to those used in the Farinograph test.

The Extensograph (AACCI 2004, Method 54–10; ICC Standard 2001, 114/1) measures dough extensibility and dough relaxation behavior. A piece of dough, prepared in the Farinograph bowl, is molded into a cylinder, clamped horizontally in a cradle, and stretched by a hook which is placed in the middle of the sample and moves downwards until rupture occurs. The measurement is repeated after three different rest times (45, 90, and 135 min). The following parameters are obtained: resistance to extension, measured 50 mm after the curve has started and related to the elastic properties; maximal resistance to extension; extensibility, which is the length of the curve; energy, given by the area under the curve. Large sample size and time requirements for both standard Extensograph and Alveograph tests have precluded their general use for breeding programs in the United States (Nash and others 2006).

Other instruments used for the evaluation of dough extension characteristics at a small scale include the *Texture Analyzer* with a *Kieffer Extensibility Rig* (Kieffer and others 1998; Mann and others 2008). Unfortunately, the parameters obtained with this approach did not correlate with the standard Extensograph method, making data interpretation difficult (Chen and others 2009). Nevertheless, the standard Extensograph and Alveograph tests cannot be used for the evaluation of wheat samples in breeding programs, where the sample size is small and number of samples is high. For this reason, Chen and others (2009) proposed a modified Extensograph method, using a smaller amount of flour.

The *Glutograph* (www.brabender.com) has been described as a method useful for testing gluten quality, such as the extensibility and elasticity of washed wet gluten, isolated from 10 g of flour with the *Glutomatic* machine (www.perten.com) (Sietz 1987). The measuring system consists of two parallel, round, corrugated plates mounted at a defined distance opposite each other. One of these plates deflects against the other, stretching the sample. Different parameters can be obtained from the Glutograph profile: shear time or stretching, corresponding to the time required to reach deflection, related to the extension of sample, and relaxation, corresponding to the recovery of the sample after 10 s, related to its elasticity. According to previous research, Sietz (1987), comparing Glutograph indices with Farinograph and Extensograph parameters, highlighted that, despite the fact that the Glutograph is a good instrument for testing gluten quality, it cannot replace more sensitive tests, but complements them as a rapid test. More recently, Alamri and others (2009) proved the potential use of the Glutograph for the evaluation of functional and technological properties of dough, assessing its suitability for replacing the other conventionally used rheological instruments. In particular, a positive and significant relationship between the Glutograph stretching parameter and specific loaf volume was shown. Starting from these considerations, the Glutograph test could potentially be useful for rapid quality tests as it is technically simple, rapid, and requires a small sample volume, so it can be used to predict the gluten strength and the end-use quality of wheat in breeding programs and in rapid screening of commercial wheat samples.

Prediction of baking performance

The final step in bread making is the baking process when the leavened dough (shaped in different ways) is transformed from the foam state to the sponge state (Cauvain and Young

2006). During this phase of the process, the gluten denatures, losing its extensibility completely and achieving elasticity, while the starch granules swell and gelatinize. The extent to which protein denaturation and starch gelatinization occur depends on several factors (such as the amount of water in the dough, the rate of heat application and the amount of heat supplied, the relative humidity within the baking chamber, and the duration of the baking process) and greatly affects the quality of the final baked products (Pagani and others 2010).

The *Mixolab* is a quite new instrument developed by Chopin Technologies (Villeneuve-la-Garenne Cedex, France) (www.chopin.fr) used to characterize the rheological behavior of dough (about 42–45% moisture content) subjected to the simultaneous action of mixing and temperature (AACCI 2004, Method 54–60.01). This instrument determines, in real time, the torque (Newton $*$ m) produced by mixing the dough between the two blades. Once the dough is formed, the device measures its behavior as a function of time and temperature. For this reason, the Mixolab provides simultaneous information about the protein and starch macromolecules (Koksel and others 2009). It is therefore possible to record the changes in consistency during mixing at room temperature and during heating (for example, from 30 to 90 °C at 4 °C/min). A typical Mixolab curve is shown in Figure 2.12. It is separated into five different stages. During stage 1, an increase in the torque is observed until an optimal dough consistency (1.1 N $*$ m Newton $*$ m; C_1) is reached and dough can resist the deformation (stability) for a time related to its protein quality (Rosell and others 2007). The dough consistency decreases with prolonged mixing, indicating weakening of the protein network (stage 2; C_2). At the beginning of the heating phase, first a decrease and then an increase in consistency are observed: the thermal weakening is related to protein quality (Rosell and others 2007). The increase in consistency at temperatures higher than 50 °C (C_3) is mainly due to starch gelatinization (stage 3). Starch granules swell and absorb water, whereas amylose molecules leach out, resulting in an increase in viscosity. At stage 4, consistency decreases (C_4) as a result of amylolytic activity (Dubat 2013). At stage 5, with the decrease in temperature, dough consistency increases as a result of gel formation (C_5), associated with the starch retrogradation phenomenon.
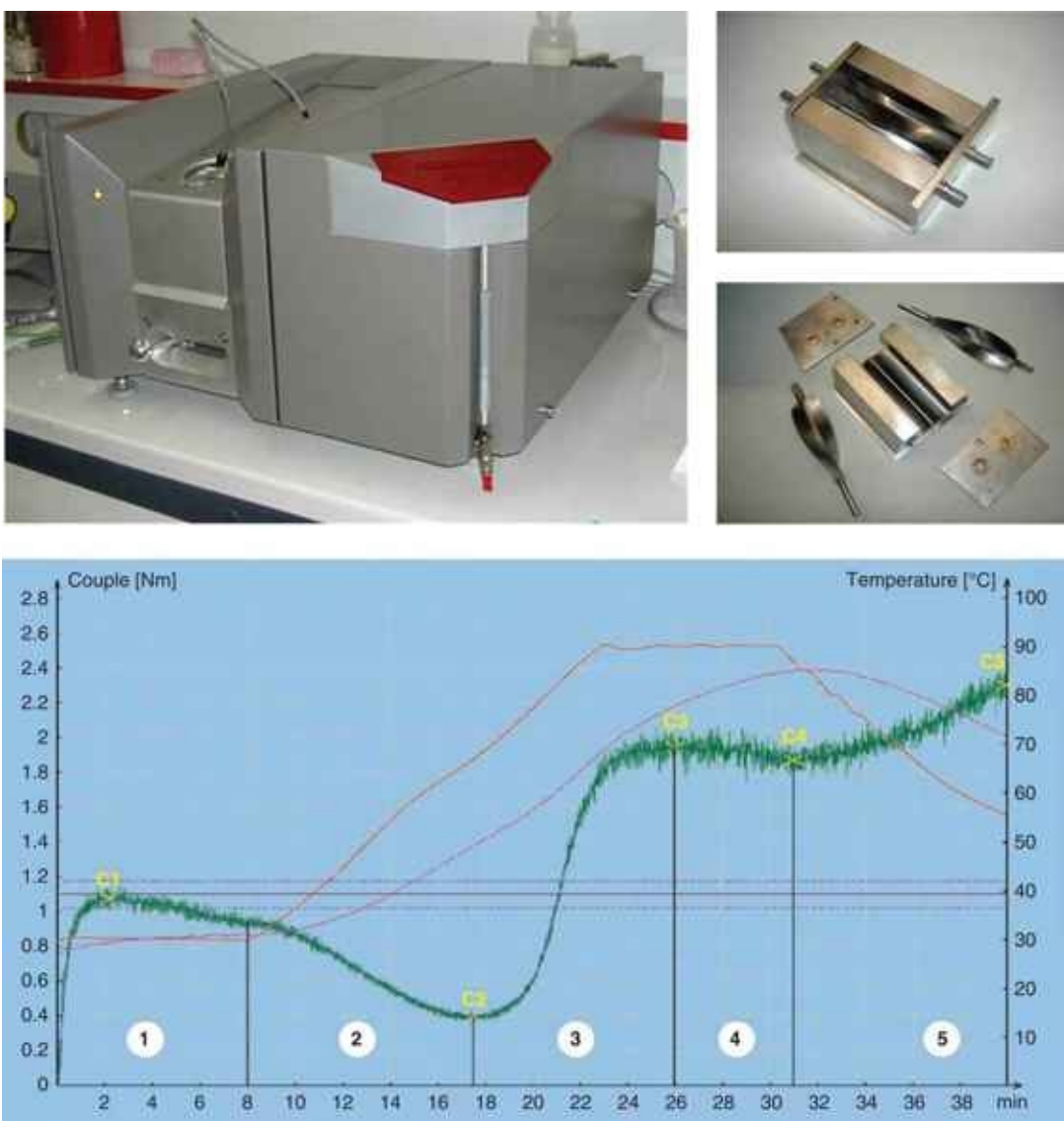
Figure 2.12 The Mixolab (top left) with paddle details (top right) and a typical curve (bottom) for wheat flour (courtesy of Chopin Technologies).

Recent studies have highlighted that the Mixolab dough development time, stability, and breakdown parameters showed a high correlation with the dough strength indices measured with the Farinograph and the Alveograph, the Zeleny sedimentation test, and with bread volume values (Koksel and others 2009). Moreover, stages 3, 4, and 5 of the Mixolab curve show strong similarity to curves obtained by the *RapidViscoAmylograph* (RVA) (www.perten.com) and by the *MicroViscoAmyloGraph* (MVAG) (www.brabender.com). It is important to consider that the Mixolab produces results with measurements taken on actual dough rather than on a suspension or slurry, like the RVA and MVAG tests.

New instrumental approaches

The methods proposed for analyzing wheat flour properties are growing because of the increased need to predict behavior during a real technological process or to evaluate on-line performances. *Near Infrared Reflectance* (NIR) spectroscopy has been proposed as a low-cost technique (per unit test) for conducting non-destructive rapid tests on small amounts of whole grain (Sissons and others 2006). Used since 1975 to screen ground wheat samples for protein and moisture content (Williams 1979), today the NIR approach is routinely used throughout the world to evaluate many compositional features of wheat. This allows breeders

to screen large numbers of lines for this key characteristic, as well as to determine moisture, dietary fiber content, kernel hardness, and rheological properties (Osborne 2007). Recently, the applications of NIR spectroscopy in the cereal sector have also been focused on the prediction of several aspects of so-called "technological quality", including flour yield, damaged starch, water absorption, dough development time, extensibility, and loaf volume (Cozzolino and others 2006; Kaddour and others 2008a, 2008b; Kaddour and Cuq 2009), even at the moment of harvest (Arazuri and others 2012). Moreover, the models had enough accuracy to predict extensibility (L), deformation energy (W), ratio P/L (Cocchi and others 2005; Arazuri and others 2012), and water absorption (Mutlu and others 2011), suggesting their beneficial use in the classification of wheat and flour samples.

The *GlutoPeak* (www.brabender.com) is a new piece of equipment proposed for the description of gluten quality. In particular, it provides a quick measurement of the aggregation behavior of gluten, as vital gluten, flour, or coarse grain. The test is carried out using small sample sizes (usually between 8 and 10 g), high water content slurries (125% water), high shear (1900–3000 rpm), and a short time (usually 10 min). A typical curve obtained by the GlutoPeak is shown in Figure 2.13. The torque trend is recorded over time and expressed in Brabender equivalents (BE). The main indices considered are the maximum torque (MT), corresponding to the peak occurring as gluten aggregates, and peak maximum time (PMT), corresponding to the time at maximum torque. Weak wheat flours are generally characterized by a rapid torque build-up to a sharply defined peak, followed by a rapid breakdown. This technique has been proposed as a tool for facilitating quality evaluations even in the early stages of breeding programs, as well as for samples which are usually blended flours, making it possible to compare all kinds of flours on one comparative scale (Kaur Chandi and Seetharaman 2012).
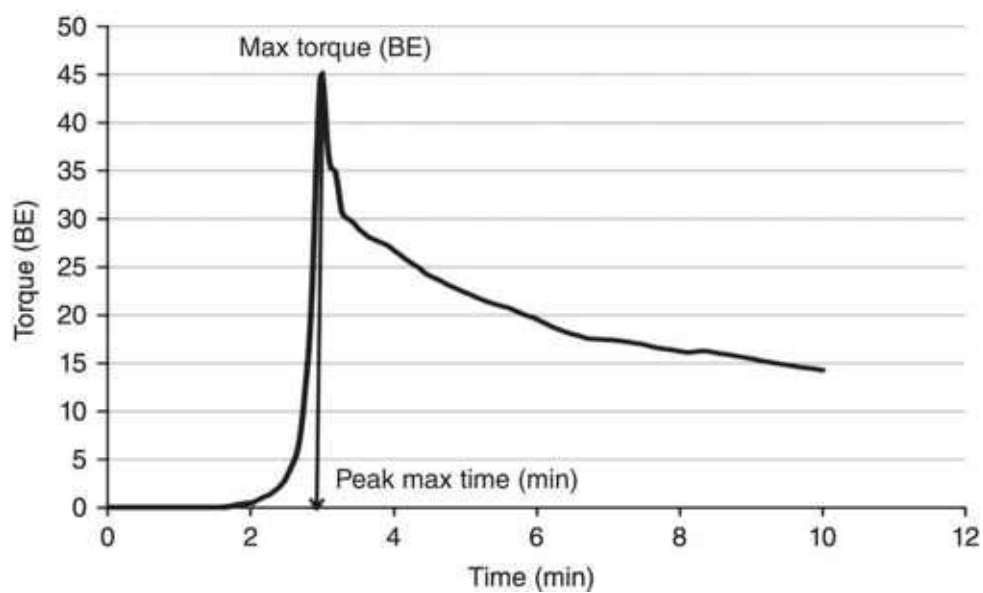
Figure 2.13 The GlutoPeak (top) with paddle detail (top right) and a typical curve (bottom) for wheat flour (courtesy of Brabender GmbH & Co. KG).

Future trends

Wheat flour, a raw material of primary importance both in the past and today, is subject to all the problems that affect a globalized food market. With grain cultivated in all the continents and modern milling techniques, millers can obtain high milling yields (lowering processing costs), and at the same time guarantee excellent hygienic and technological characteristics. Nevertheless, the increasing demand for flour with heightened nutritional characteristics, thanks to the recovery and exploitation of the natural components in the wheat kernel, has given rise to numerous studies on wholegrain flour and products. There are two main problems which require effective and economically practical solutions, and they can be summarized as prolonged shelf-life and improvement of the technological properties of wholegrain flours. Until the middle of the 20th century, flour was a true "zero km" product: the grain was milled in small mills and in small quantities to satisfy short-term demands, and had very limited storage times. Today, the mills work thousands of tons a day, and distribute the product hundreds – if not thousands – of miles away. It is therefore indispensable to research mild and friendly technologies that will give a prolonged shelf-life to wholegrain flours. Furthermore, it is important to improve the technological performances of wholegrain flours in order to obtain bread and other end-products with sensory characteristics similar to those from refined flours.

Acknowledgments

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3
Wheat Flour: Chemistry and Biochemistry

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Foreword

Wheat kernels include starch and non-starch polysaccharides along with gluten and non-gluten proteins that are all essential to plant development. Proteins provide both the enzyme pool and the nitrogen source required for sprouting, a process in which starch is used as the main source for energy and growth before photosynthesis begins. More relevant to our purposes here, many unique properties of wheat starch and proteins have been exploited for converting wheat grains into a broad variety of foods. In particular, the complex protein system generally defined as gluten has a number of quite peculiar features that are fundamental for transformation into food, and for defining the overall quality of bakery products. The amount and quality of gluten in wheat flour affect dough formation and development, and the textural and physical characteristics of baked products. Genetic selection has been aimed at improving the content of specific performance-related proteins, as well as grain yield and other agronomically relevant traits. Starch has received less attention, but the suitability of a given variety for a specific transformation is now known to be strongly influenced by more or less specific interactions among molecules and macromolecules present in the various types of matrix that are encountered in baking. Understanding these interactions has recently moved from phenomenological observations towards defining and understanding an increasing number of issues at the molecular level. Thus, structural information derived from chemistry or biochemistry needs to be complemented by physical measurements and by the more traditional indexes used to define the quality of the products, including sensory evaluation.

Wheat proteins

Classification

Wheat proteins account for about 10–15% of the grain dry weight and are the most important factors affecting the technological properties of wheat. The analysis and classification of wheat proteins has a long and enchanting story, as the first scientific literature report goes back more than 250 years (Beccari 1745), although wheat proteins remain the subject of many studies addressing the relationships between protein quality and the unique properties of flour.

A common and still used method of classification of wheat grain proteins was developed in the early 20th century by Osborne (Osborne 1907). Based on solubility, Osborne classified proteins into four major types: albumins (soluble in water or diluted salt), globulins (soluble in diluted salt, but insoluble in water), gliadins (soluble in aqueous alcohols), and glutenins (insoluble in aqueous alcohols). Albumins and globulins constitute approximately 20% of the endosperm protein and play a role in cellular metabolism, development, and response to environment. Most of the endosperm protein (80%) are gliadins and glutenins, together also known as prolamines, because of their high content of proline and glutamine. Prolamines have been also classified as sulfur-rich (α/β-, γ-gliadins, B- and C-low molecular weight glutenins) or sulfur-poor (ω-gliadins and high molecular weight glutenin subunits (HMW-GS) (Shewry and Tatham 1990).

The classification and distribution of main wheat protein, based on selective extraction, is schematized in [Figure 3.1](#). Buffered saline solubilizes albumins and globulins, which may be further subdivided into chloroform/methanol soluble (*CMs*) and insoluble (*CMins*) proteins (Rodriguez-Loperena and others 1975; Salcedo and others 1978). The water insoluble pellet consists largely of gluten. Aqueous 60% ethanol extracts gliadins (α/β-γ and ω-gliadins), whereas the residue treated with a reducing buffer/propanol mixture (50% 1-propanol containing 1% DTT) contains glutenins. These latter may be further fractioned by increasing 1-propanol to 60% (that precipitates high molecular weight fractions (HMW) and further to 65, 70, 75% for precipitation of low molecular weight fractions (LMW) (Verbruggen and others 1998; Masci and others 2002). The insoluble pellet in 50% 1-propanol mainly includes starch, but also contains minor amounts of detergent-soluble proteins (that is, soluble in diluted SDS, Triton, and the like).
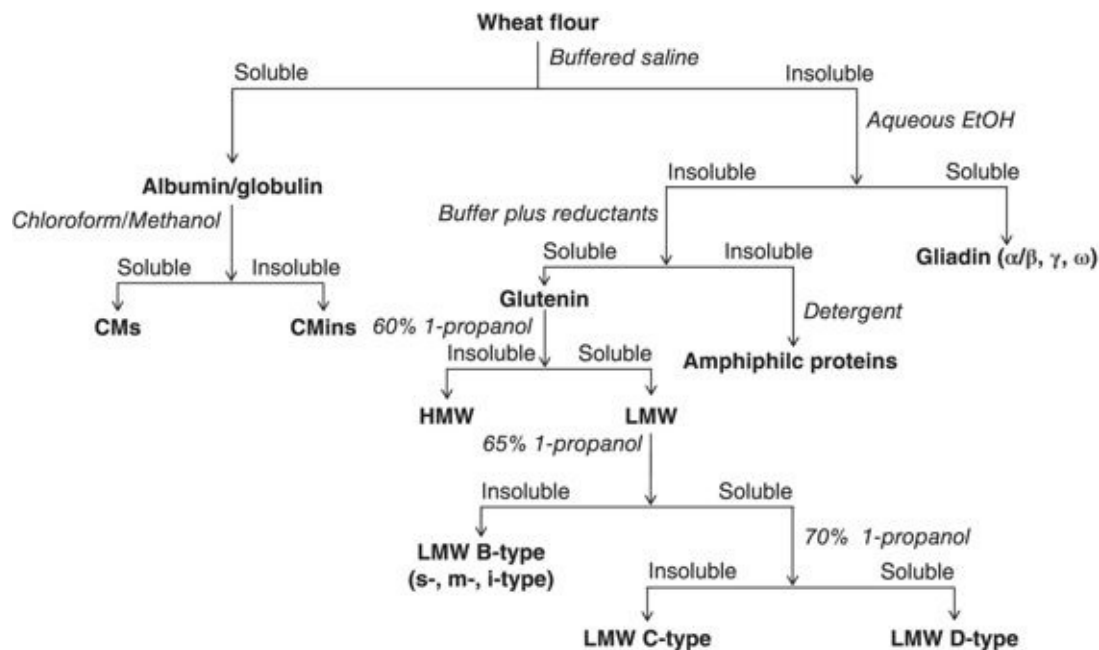
Figure 3.1 Protein fractions in wheat flour.

Non-gluten proteins

Non-gluten proteins make up a minor percentage of endosperm proteins and play important roles in metabolism. These proteins include salt-water soluble and detergent-soluble fractions. The first are albumin and globulin, of which most are smaller than 25 kDa (Veraverbeke and Delcour 2002). Proteomic analysis based on two-dimensional gel electrophoresis (2DE) and mass spectrometry (MS) showed that more than 2000 spots can easily be extracted from flour with buffered saline (Islam and others 2003; Skylas and others 2000, 2005). Among these, α-amylase inhibitors, serpins, and purothionins are predominant (Shewry and others 1984; Buonocore and others 1985; Garcia-Maroto and others 1990; Østergaard and others 2000).

Enzymes

Most of the enzymes required for plant growth are not synthesized until germination. This has been exploited in baking through the use of malt as a source of hydrolytic enzymes that act on starch, proteins, and non-starch polysaccharides and affect their behavior in various processing steps. However, differences in genetic traits and in storage conditions, as well as agronomical issues, may affect the content of these same activities in the original flour (Joye and others 2009). In practice, this requires fine tuning of the process itself, in particular when enzymes from other sources are added. The most relevant endogenous enzyme activities include representatives of the α-amylase and β-amylase families. These enzymes act on amylose and amylopectin with a different mechanism. Alpha-amylase is an endoenzyme, that splits linear unbranched regions of starch into smaller molecules. It only acts on soluble or damaged starch, and its products may represent the substrate for other enzyme activities that split out maltose (β-amylase) or glucose (glucoamylase) from the non-reducing ends of these polymers, providing nutrients for yeast and sugars relevant to sensory traits (for example, by promoting Maillard-type reactions). In general, amylolytic activities lower dough viscosity, increase the fermenting power and the loaf volume, and have a positive impact on the product shelf-life.

Other enzymes that may have a profound impact on dough properties or on those of the products are acting on non-starch polysaccharides (pentosans, xylans, and other components usually classified collectively as "hemicelluloses"), or on proteins. Proteases may have a negative effect (as they may weaken the gluten network, as explained in a later section of this chapter), but may affect in a positive way some peculiar features, such as the capability to retain a given shape upon baking, or the formation of colored compounds on the crust. However, most of these activities are typically present in very low amounts in non-sprouted grains (Dornez and others 2009).

Although in low abundance, enzymes that act on lipids (most notably, lipases and lipoxygenases) are also relevant to the dough properties. Lipases act on triglycerides by converting them into amphiphylic diglycerides that may act as surfactants and modify the behavior of endogenous or added lipids. Lipoxygenases are of interest because they act on unsaturated compounds in flour (fatty acids, but most notably carotenoids) and because by-products of their activity may affect number of cross-links in gluten proteins.

Enzyme inhibitors

This class of proteins, and in particular α-amylase inhibitors, may account for two-thirds of all albumins. These proteins inhibit mammalian and insect enzymes but not the endogenous α-amylases, implying a protective role against predators (Carbonero and García-Olmedo 1999). These proteins are selectively soluble in chloroform/methanol mixtures ([Figure 3.1](#)), and display molecular masses of 12, 24, and 60 kDa as a consequence of the presence of monomeric (WMAI-1,2), homodimeric (WDAI-1,2,3), and tetrameric form. The last comprises a single copy of two subunits (WTAIC-CM1/2 and WTAI-CM16/17) and two copies of a third subunit (WTAI-CM3B/D). Each α-amylase inhibitor, includes 10 cysteine residues and forms 5 disulfide bonds, except WDAI-1 that contains 9 cysteines (Carbonero and García-Olmedo 1999; Poerio and others 1991; Oda and others 1997). Members of the family of α-amylase inhibitors have an important impact on human health as they are the major group of wheat protein responsible for respiratory and food allergy, as discussed below.

Amphiphilic proteins

Most amphiphilic proteins are lipid-binding proteins, often strongly linked to technological aspects, such as dough forming properties (Amiour and others 2002). An important group of 15 kDa proteins, named friabilins, are present at the surface of starch granules in larger amounts in soft wheat than in hard wheat (Greenwell and Schofield 1986; Jolly and others 1993). The two major polypeptides of the friabilin fraction were found to be identical to two isoforms of puroindolines – puroindoline-a (Pin-a) and puroindoline-b (Pin-b) (Gautier and others 1994). These basic (pI = 11) and cysteine-rich proteins, soluble in Triton X-114, possess a unique tryptophan-rich hydrophobic domain, which is responsible for their strong affinity for lipids, and are encoded in the Hardness (Ha) 5 locus, on the short arm of chromosome 5D, the major locus controlling texture. Pin-a has been associated with softness, and Pin-b with hardness. The presence of both puroindolines in their `functional' wild state results in a soft grain texture. When either one of the puroindolines is absent or altered by mutation, a hard texture results. Indeed, durum wheat does not contain puroindolines (Morris 2002). Pin-a binds to wheat phospholipids and glycolipids, and Pin-b only binds to negatively charged phospholipids.

Gluten proteins

Gluten proteins are present in the mature wheat grain endosperm where they form a continuous matrix around the starch granules. Gluten contains hundreds of protein components which are present either as monomers (gliadin) or in polymers of various complexity linked by interchain and intrachain disulfide bonds (glutenin) (Wieser 2007). Comprehensive annotation of the gluten protein is challenging, due to extensive polymorphism. Genes encoding gluten proteins probably originated by duplication and translocation, which results in insertion and deletion of peptide sequences as well as amino acid substitutions (Shewry and others 1986).

The gluten protein heterogeneity can be rationalized with the help of analytical techniques such as sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE), 2DE (Mamone and others 2005), high performance liquid chromatography (HPLC), capillary electrophoresis (CE) (Di Luccia and others 2009), and MS. In particular, MALDI-TOF (Matrix Assisted Laser Desorption-Time Of Flight) and ESI (Electrospray Ionization) MS have proved their value in the characterization of gluten proteins (Mamone and others 2009a).

Gliadins

Gliadins are monomeric proteins with a relevant role in the development of the gluten intermolecular network through the formation of hydrogen bonds, hydrophobic bonds between non-polar amino acid side chains, and through thiol–disulfide exchange. Gliadins also interact with the flour lipids or with added lipids and determine dough extensibility (Khatkar and others 2002; Veraverbeke and Delcour 2002).

Gliadins are traditionally subdivided into α/β-, γ, and ω fractions according to their mobility in polyacrylamide gel electrophoresis at acid pH (A-PAGE). Although migrating differently in A-PAGE, α- and β-gliadin have a very similar sequence: a short non-repetitive N-terminal domain; a central domain lacking cysteine residues and formed by repetition of two Pro- and Gln-rich sequences (the Pro-Gln-Pro-Gln-Pro-Phe-Pro heptapeptide and the Pro-Gln-Gln-Pro-Tyr pentapeptide); a long C–terminal domain containing six Cys and most of the charged amino acids (Figure 3.2). Alpha- and β-gliadin are currently considered a single gliadin (α/β type) (Kasarda and others 1987). Also, γ-gliadins are formed by three different regions (Bartels and others 1986): a short N-terminal domain; a repetitive central domain formed by repetition of a Pro- and Gln- rich sequence (as the Pro-Gln-Gln-Pro-Phe-Pro-Gln heptapeptide); and a C-terminal domain with eight Cys and most of the charged residues (Figure 3.2).
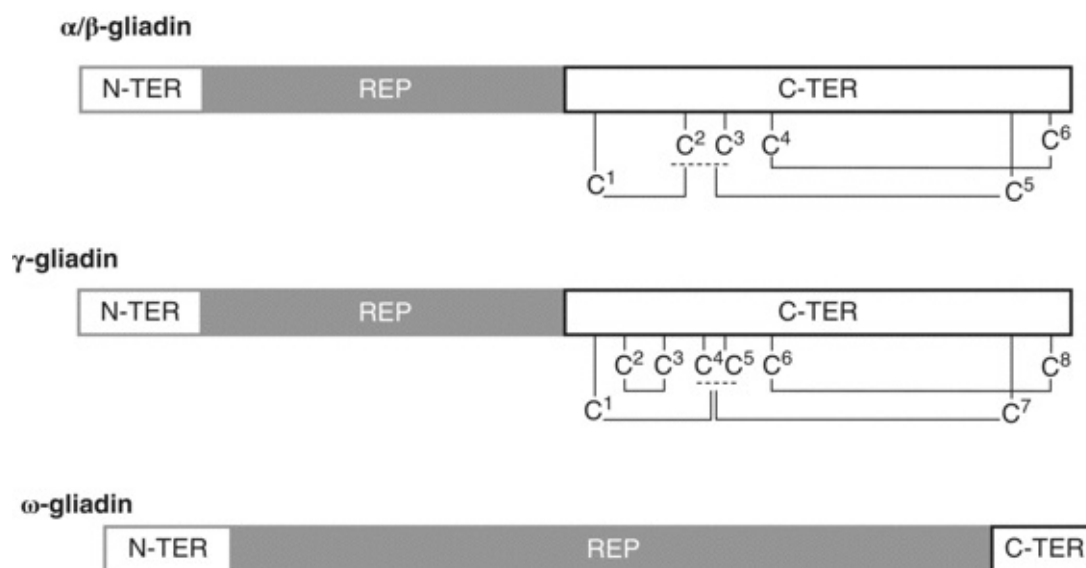
Figure 3.2 A schematic view of the structure of the most common gliadins.

The amino acid composition and structure of ω-gliadins (44–74 kDa) are totally different from that of α/β- and γ-gliadins. No cysteine is present in ω-gliadins, which are essentially a single repetitive domain where 80% of the amino acid residues are glutamine, glutamic acid, proline, and phenylalanine (Figure 3.2) (Hsia and Anderson 2001).

Several cDNA-deduced amino acid sequences of gliadins have been reported (Shewry and others 1986). Because of extensive polymorphism, however, these have hardly matched at the protein level. Using SDS-PAGE or HPLC (Rocher and others 1995), components may co-migrate in a single band or peak, but underestimation of the number of species can be avoided by coupling HPLC to ESI-MS (LC-MS) (Mamone and others 2000).

Glutenins

The glutenin fraction consists of protein aggregates from about 60 000 to more than 10^6 Da. Following reduction of interchain and intrachain disulfide bonds, the glutenin subunits show a solubility in aqueous alcohols similar to gliadin. Based on SDS-PAGE mobility, glutenin subunits have been divided into high molecular weight (HMW) and low molecular weight (LMW) (Figure 3.3) (Wieser 2007).
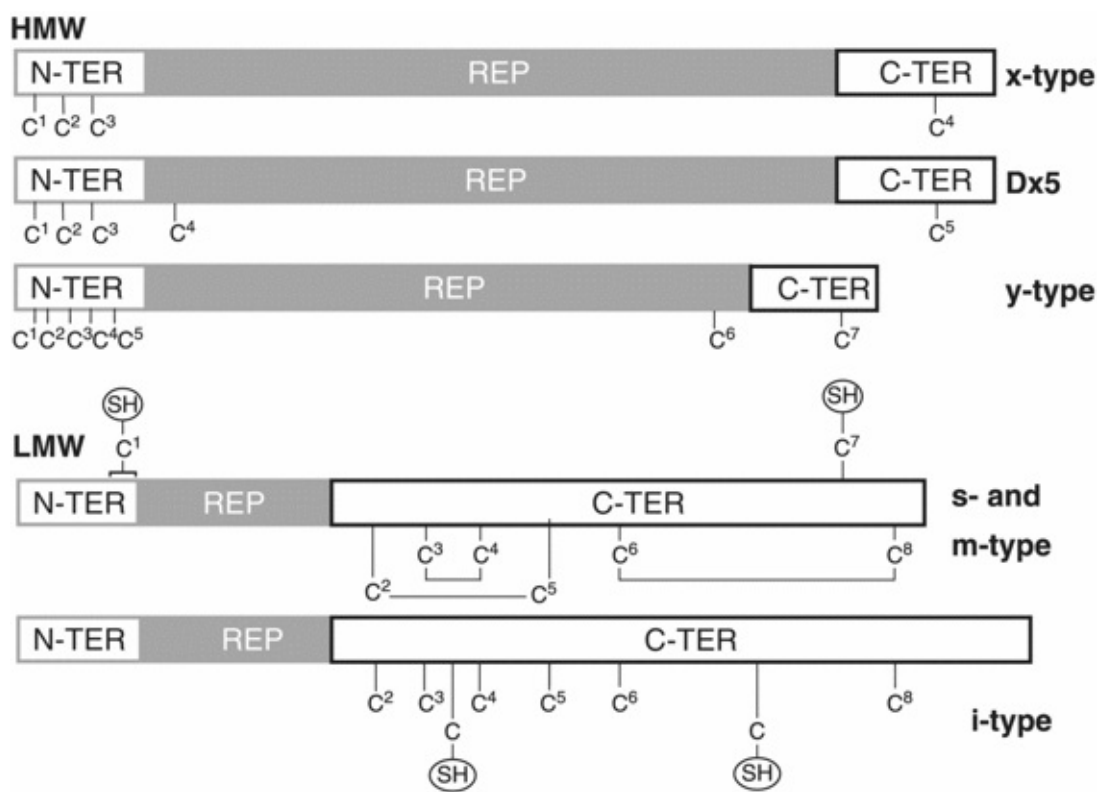
Figure 3.3 A schematic view of the structure of the most common glutenins.

High molecular weight glutenins

HMW-GS represents minor components (5–10%) within the gluten protein family, but dough properties are reportedly strongly influenced by the relative amount of HMW-GS (Field and others 1983). The HMW-GS are encoded by genes at loci located on the long arms of chromosomes 1A, 1B, and 1D designated as Glu-1 (Glu-A1, B1 and Glu- D1) (Payne 1987). Each locus contains two tightly associated genes, encoding subunits designated x-type and y-type (83–88 kDa and 67–74 kDa, respectively). Because of the silencing of some Glu-1 genes, only 3–5 HMW subunit genes are expressed in various wheat bread cultivars. In particular, HMW-GS type 1Dx and 1Dy and HMW-GS type BX are always expressed, whereas only some cultivars express HMW-GS type 1By and HMW-GS type 1Ax. In contrast to the situation for tetraploid and hexaploid cultivated wheat, the HMW-GS type 1Ay may be expressed in diploid wheat (*T. monococcum*), and in wild tetraploid wheat (*T. turgidum* ssp. Dicoccoides) (Waines and Payne 1987; Levy and others 1988), although a Swedish wheat hexaploid cultivar was also found to express 1Ay1 (Margiotta and others 1996).

More than 40 HMW subunit genes have been characterized by genomic analysis, including the complete set of genes from the bread wheat cultivar Cheyenne (Anderson and others 2002). These studies have shown that mature HMW-GS consist of three structural domains (Figure 3.3) comprising a non-repetitive N-terminal domain, (80–105 residues), repetitive central domain (480–700 residues), and a C-terminal domain of 42 residues (Shewry and others 1992). The N- and C-terminal domains are characterized by the frequent occurrence of charged residues and by the presence of most of the cysteine residues. The central domain contains repetitive hexapeptides units (QQPGQG) as a backbone with inserted hexapeptides (for example YYPTSP) and tripeptides (for example QQP or QPG). The N- and C-terminal domains contain cysteine residues that form interchain and intrachain disulfide bonds (Shewry and others 2002). In the majority of HMW sequences, the x-type subunit includes 4 cysteine – 3 at the N-terminal and one at the C-terminal (Shewry and others 1992) (Figure

). The y-type subunits has 7 cysteines – 5 in the N-terminal domain, 1 within the repetitive domain, and 1 close to the C-terminus.

The number of cysteine residues is of particular interest as disulfide bonds play an important role in determining gluten elasticity through formation of larger glutenin polymers using intermolecular disulfides. The bread-making quality of wheat genotypes is determined by the expression of specific HMW-GS genes. For instance, 1Dx5 subunits are thought to have a branching effect in the glutenin macropolymers owing the additional cysteine located in the central domain (Figure 3.3). In contrast, cultivars containing the subunit 1Bx20, which lacks 2 cysteine in the N-terminal region, have poor processing quality (Shewry and others 2002).

MALDI-MS of purified HMW subunits gave results consistent with their cDNA-derived sequences. Mapping tryptic peptides of HMW subunits by MS ruled out the presence of glycosylation or other post-translational modifications, making the HMW glutenins pattern comparatively simple (Mamone and others 2009b).

Low molecular weight glutenins

Based on SDS-PAGE mobility, LMW-GS are classified into B (42–51 kDa), C (30–40 kDa), and D-types (55–70 kDa) (Payne and Corfield 1979), the B-type being the most abundant LMW-GS (Payne and others 1985). LMW-GS differ significantly in their structure and function. D-type proteins correspond to a ω-gliadin-like protein with an additional cysteine that allows for interchain disulfide bond formation in the glutenin polymer (Masci and others 1993, Masci and others 1999). C-type have a structure similar to α/β and γ-gliadin, and also contain an extra unpaired cysteine residue. The presence of an odd number of cysteine residues makes the C- and D-type behave as terminators of the growing glutenin polymer chains, which is presumed to have a negative effect on flour quality (Tao and Kasarda 1989).

B-type glutenins are "typical LMW-type" which can be subdivided in LMW-s, LMW-m and LMW-i types, on the basis of the first amino acid in the mature polypeptide (serine, methionine, or isolecucine, respectively) (Figure 3.3). LMW-s type subunits are the most abundant and their size (35–45 kDa) is higher than that of LMW-m type subunits (30–40 kDa) (Tao and Kasarda 1989; Masci and others 1995). The sequences of LMW-s and LMW-m consist of a short N-terminal region (13 residues) including the first cysteine residue, a repetitive domain (70–186 residues) rich in glutamine, and a C-terminal region (about 180 residues) containing 7 cysteine residues. The repetitive domain is based on the single repeat motif PPFSQQQQ followed by a variable number of glutamine residues. The variation in size of the LMW subunit depends largely on the length of the repetitive domain. In total, mature LMW-m and LMW-s contain 8 cysteine, of which the 1st and 7th are involved in intermolecular disulfide bonds, whereas the others participate in intramolecular bonds.

Finally, LMW-i type are similar to LMW-s and LMW-m, but their N-terminal region starts directly with the repetitive domain after the signal sequence, and ISQQQQ appears as the only deduced N-terminal sequence of all LMW-i type genes isolated so far. Although the N-terminal region is missing, LWM-i contain the typical 8 cysteine residues, all distributed in the C-terminal domain (Figure 3.2) (Cloutier and others 2001; Ikeda and others 2002) and all involved in interchain disulfide bonds. The ability of LMW to form a variable number of intermolecular disulfide bonds, define their role as chain extenders or chain terminators. LMW B-type forming two interchain disulfide bonds allows, upon incorporation into a protein network, the extension of glutenin polymers ("chain extenders"). LMW C-type and D-

type, once incorporated into a polymer chain, behave as chain terminators as they block further extension of the disulfide network because they lack the additional free cysteines required for forming further interchain linkages.

In contrast to the low number of HMW, the protein profile of LMW is highly heterogeneous. Electrophoresis and HPLC analyses show a complex pattern of proteins in the 30–40 kDa range (Bietz and Simpson 1992; Mamone and others 2009a; Muccilli and others 2010). MALDI TOF-MS of LMW has enabled characterization of new subunits (Masci and others 1995; An and others 2006) and their Cys pattern (Masci and others 1998). LC/ESI–MS has enabled characterization of about 40 B- and C-type subunits and of their Cys pattern (Muccilli and others 2005).

Other gluten proteins

Extraction of glutenin in disulfide-reducing buffers evidenced the presence of proteins not belonging to the glutenin family. Serpin Z1A and β-amylase have been identified by 2DE of glutenin extracts (Mamone and others 2009b), and evidence of disulfide bonds between β-amylase and LMW-GS has been also reported (Peruffo and others 1996), likely as a consequence of their incorporation in the glutenin network through inter-protein disulfide bonds.

An important class of protein not strictly classified as wheat gliadin or glutenin is that of the avenin-like proteins (ALPs), a small family of wheat storage proteins having a weak sequence similarity to the oats avenins. They occur in two isoforms, ALP type-A and ALP type-B. ALP type-A contains a total of 14 cysteine residues (Kan and others 2006). Extraction of ALP type-A monomer under non-reducing conditions means that protein was not engaged in the gluten polymer through S–S bonds. In contrast, ALP type-B proteins contain 19 (type-B-1, -3 and −4) or 18 cysteines (type-B-2), and do not correspond to any known protein sequence. They differ from ALP type-A for a ~120-residue insertion, corresponding to a duplicated N-terminal region (Kan and others 2006). The genes of ALP type-B have been characterized in 23 species of Triticaceae (Chen and others 2008). The detection of ALP type-B in the GS fraction and its high content of cysteine residues suggest that it could be integrated via interprotein disulfide bonds within the glutenin polymer, possibly contributing to the functional quality of gluten (Mamone and others 2009b; De Caro and others 2010).

Adverse reactions to wheat proteins

Wheat proteins are also known to be responsible for a number of adverse reactions in humans, including intolerances (notably celiac disease) and allergies (respiratory and food). More recently, intolerance to gluten proteins – also defined as gluten sensitivity – has been proposed to represent a separate pathology (Catassi and Gobellis 2007).

Allergy is a hypersensitivity reaction of immunological origin producing a pathological condition in response to stimuli that are normally well tolerated by healthy individuals (Johansson and others 2004). Allergic reactions can be provoked by a variety of challenges, including ingestion of foods. They are a consequence of inappropriate immune responses, resulting in inflammatory reactions and tissue damage and almost invariably involve generation of an immunoglobulin E (IgE) response towards the offending agent, defined as an allergen. Wheat (as well as other cereals) have been found to trigger two types of IgE-mediated allergic diseases: respiratory allergy (bakers' asthma), and food allergy. The former is a frequent occupational allergy resulting from the inhalation of flour and dust during grain processing. Western blotting and immunoblotting analyses showed that the sera of baker's-asthma patients react with a wide range of wheat proteins, including gliadins, glutenins, serpins, thioredoxins, agglutinins, and enzymes (α- and β-amylases, peroxidase, acyl CoA oxidase, glyceraldehyde-3-phosphate dehydrogenase, and triosephosphate isomerase) (Tatham and Shewry 2008.) Among these, α-amylase inhibitors are considered the major wheat proteins responsible for this syndrome (Gomez and others, 1990). In particular, a low-abundance glycosylated form of WTAI-CM 16 (termed WTAI-CM16*) showed the strongest IgE-binding response (Sanchez-Monge and others, 1992).

The second well-characterized form of allergy is wheat-dependent, exercise-induced anaphylaxis (WDEIA, induced by the ingestion of a causative food and by subsequent physical exercise), for which ω-5-gliadins are considered predominantly responsible (Morita and others, 2003). Measurement of serum IgE antibodies against ω5-gliadin has been proposed as a WDEIA marker (Matsuo and others 2004), but other proteins react with IgE from WDEIA patients, including gliadins and glutenin subunits (Maruyama and others, 1998). Immunodominant epitopes in ω5-gliadins consist of short glutamine-rich and proline-rich sequences in the repetitive domains (Matsuo and others 2004, Matsuo and others 2005; Battais and others 2005).

Celiac disease (CD) is the result of a series of complex mechanisms involving genetic and environmental factors (Sollid 2000). Genetic factors play a basic role in CD, as proven by familiar aggregation of diagnosed cases (5–15%) and by the 85% concordance in homozygous twins. Linkage studies clearly showed the association of CD with defined alleles of the class II major histocompatibility complex (HLA). However, CD is triggered only upon the introduction of gluten-containing foods in the diet of susceptible individuals. Intestinal digestion of gluten proteins produces several peptides that can stimulate either adaptive or innate immune responses (Gianfrani and others 2005).

The adaptive immune response has been studied through the identification of specific immunogenic peptide sequences which are presented by HLA-DQ8 or HLA-DQ2 to gluten-sensitive CD4+ T-cell lymphocytes. Binding of gluten peptides to the HLA molecules becomes more relevant when a single glutamine residue is deamidated to glutamic acid by tissue

transglutaminase (Molberg and others 1998; Arentz-Hansen and others 2000). Following gluten recognition, prevalently pro-inflammatory cytokines are released, leading to profound tissue remodeling (Sollid 2000). Although at least 50 T-cell stimulatory gliadin and gluten epitopes in native or deamidated form have been identified, a 33-mer peptide released from α2-gliadin through gastric and pancreatic enzyme digestion is nowadays considered the most immunogenic, since it includes 6 overlapping epitopes. The 33-mer peptide is also highly resistant to further digestion by intestinal brush-border membrane (BBM) enzymes, so that it could reach the underlying *lamina propria* (LP), playing a central role in the pathogenic cascade of CD (Shan and others 2002).

Gliadin-derived peptides elicit an innate immune response in professional antigen-presenting cells (monocytes, macrophages, and dendritic cells) that predominantly activates intraepithelial lymphocytes and intestinal epithelial cells (Londei and others 2005; Maiuri and others 2003). Contrary to adaptive immune response, innate immune response has only recently begun to receive attention. Almost all research on these topics has been performed using a model peptide 31–43 (LGQQQPFPPQQPY) (Shan and others 2002), but it has been demonstrated that this peptide is encompassed in a longer sequence (that is, 31–55, LGQQQPFPPQQPYPQPQPFPSQQPY) which is resistant to gastropancreatic and subsequent BBM enzyme digestion even after prolonged exposure (Mamone and others 2007).

Intolerance to gluten has recently been proposed to represent a separate pathology with respect to CD. Gluten sensitivity is defined as an adverse reaction to gluten in which neither allergic nor autoimmune mechanisms are involved (Catassi and Gobellis 2007). Gluten sensitive individuals develop an adverse reaction when eating gluten-containing products, but usually – at difference from celiac disease – there is no small intestine damage. While the gastrointestinal symptom in gluten sensitivity may resemble those associated with celiac disease, the overall clinical picture is generally less severe and is not accompanied by the concurrence of an autoimmune response

Polysaccharides

Starch

Starch is the most abundant carbohydrate in wheat grains, (75–80% of the dry weight; Stone and Morell 2009), and the starch content seems to be inversely related to the protein content. Soft wheat varieties, in general, have higher starch contents than hard ones (Shelton and Lee 2000). In mature wheat, two distinct classes of granules occur that differ in size and shape: large lenticular granules (A-type, about 20–35 μm), and small spherical granules (B-type, 2–8 μm diameter).

Starch is usually referred to as a semicrystalline material and a "fringed micelle" model has been proposed in which microcrystalline regions/layers connect to amorphous regions/layers of flexible chain segments (Slade and Levine 1987). Starch is composed of amylose and amylopectin polymers, based on anhydroglucose units and chemically similar, but differing in the degree of branching of the d-glycosyl units. Amylose is an essentially linear molecule – although linear chains can form helical structures – consisting of $\alpha(1–4)$-linked d-glycosyl units with a degree of polymerization (DP) in the range of 500–6000 glucose residues. Amylopectin also contains $\alpha(1–4)$ d-glucosyl chains, but branches occur every 20–25 residues due to $\alpha(1–6)$ linkages. Amylopectin is a very large molecule with a DP ranging from 3×10^5 to 3×10^6 glucose units. Three types of chains are present: A-chains, consisting of α-1,4-linked glucose units; B-chains, consisting of α-1,4- and α-1,6-linked glucose units, and C-chains, showing both types of linkages and an aldehyde function at the C1 end. The ratio of the A- to B-chains is usually from 1 : 1 to 1.5 : 1 (Whistler and Deniel 1984). The amylose/amylopectin ratio differs among starches, but amylose and amylopectin in wheat are typically 25–28% and 72–75%, respectively (Van Hung and others 2006). Exceptions are the starches from mutant grain varieties containing high amounts of amylose, or starches which only virtually contain amylopectin ("waxy starches").

Wheat starch helps determine the appearance, structure, and quality of many food products. Its major uses in food application are connected with gelatinization, pasting, and retrogradation, which underlie starch functionality. During processing, starch dispersions are subjected to combined heating and shearing effects that affect their rheology and the final characteristics of the product (Cornell 2004; Mason 2009). Native starch granules are insoluble in cold water, but when temperature is increased – and water is present – starch in the insoluble granules loses its molecular organization and undergoes irreversible changes in its properties.

The temperature at which birefringence is first lost is the gelatinization temperature (53–64 °C in wheat starch, lower than in most starches) (BeMiller and Whistler 1996), and depends on concentration, granule type, and heterogeneity within the granule population (Atwell and others 1988). Because of the practical relevance of starch gelatinization (Cornell 2004), several methodologies have been deployed to study its mechanism, including microscopy (Liu and others 2002), differential scanning calorimetry (Donovan 1979), X-ray diffraction (Nara and others 1978), nuclear magnetic resonance (NMR) (Cooke and Gidley 1992), and Fourier transform infrared (IR) spectroscopy (Goodfellow and Wilson 1990).

Pasting is defined as the state following gelatinization of starch. When starch granules are heated in the presence of water, the granules absorb a large amount of water and swell to many times their original size. The flow behavior of a starch slurry changes markedly as the suspension becomes a dispersion of swollen, partially disintegrated, and dispersed granules. A rapid increase in viscosity occurs when a sufficient number of granules swell, and the temperature at the onset of the viscosity increase is known as the pasting temperature. Swelling over a broad temperature range indicates granule heterogeneity. The starch paste is described as a two-phase system where swollen granules are dispersed in a continuous phase of entangled amylose molecules (Ring 1985; Mason 2009). Peak viscosity occurs at the equilibrium between swelling and polymer leaching. The increase in viscosity continues to a maximum when most granules burst and form a network of interlocking chains. Pasting properties of starch are governed by the concentration, the heating rate, and the presence of other food components (Mariotti and others 2005). If the amylose phase is continuous, aggregation with linear segments of amylopectin upon cooling results in the formation of a strong gel.

Upon cooling, the amylose chains in starch reassociate and form a gel. This process is referred to as *gelation* or *retrogradation,* and involves formation of ordered structures – such as double helices – during storage (Atwell and others 1988). Retrogradation is important as it can be a desired end point in certain applications, but it also causes bread staling and instability in starch pastes. The rate of retrogradation is influenced by the botanical source (for example, cereal starch in contrast to tuber starch), by the amylopectin structure (chain length and distribution), and by the amylose : amylopectin ratio. In general, retrogradation takes place in two stages. The first and fastest stage (< 1 day) is the formation of crystalline regions from retrograded amylose (Goodfellow and Wilson 1990). The second stage involves the formation of an ordered structure within amylopectin (Gudmundsson 1994). In particular, amylose is able to form double helical association of 40–70 glucose units, whereas amylopectin crystallization occurs by association of the outermost short branches (for example, DP = 15) (Ring and others 1987).

Non-starch polysaccharides

Cellulose and non-cellulosic polysaccharides constitute, along with modest amounts of oligosaccharides, the majority of non-starch polysaccharides in wheat flour. From a nutritional standpoint, these polysaccharides are taken as constituents of the "edible fiber" fraction, whose importance in the diet has been underscored by countless studies.

The non-cellulosic polysaccharides in cereals – collectively referred to as hemicellulosic materials – may account for up to 2–8% of total carbohydrates. In order of relative abundance, they include arabinoxylans, (1–3),(1–4)-beta-glucans, pectins, and arabinogalactans (Tharanathan 2002). These flour components are important in the baked goods industry because of their water-buffering capacity. Arabinoxylans are most effective at absorbing water, and therefore at influencing water balance and water transfer among proteins and starch, with effects (discussed in previous sections) on the rheological properties of dough and on the retrogradation of starch. Arabinoxylans are often found complexed with ferulic acid esters in ways that may affect product behavior (Saulnier and others 2007). In contrast, the minute amounts of cereal pectins and arabinogalactans do not contribute substantially to flour functionality. Beta-glucans are of interest as biological

response modifiers, given their role in modulating the immune response (Muralikrishna and Rao 2007). Oligosaccharides also show biological effects that are relevant to the development of probiotic flora, although their content in mature kernels is very low (Iametti and others 2006).

The water-buffering ability of hemicelluloses may be modulated and increased by using enzymes, which are often present in various "improvers". These mixtures of hydrolases break down larger hemicellulosic components (along with cellulose itself, if present) increasing their water-holding capacity and releasing some of the phenolics embedded in their structure, along with minor components that are present as glycosides.

Interactions within components

Protein–water interactions

Proteins are deposited in most grains in an almost dry state and in a very compact conformation. The abundance of glutamine residues in both gliadins and glutenins minimizes protein interactions with water, and the abundance of proline residues prevents the formation of extensive secondary and tertiary structures within some of the gluten proteins, while providing appropriate structural flexibility once water is added to these proteins.

Proteins – including those in gluten – and non-starch polysaccharides other than cellulose are the components of flour that first take up added water. Interaction with water (solvation of charged or hydrophylic groups on amino acid side chains) leads to significant structural changes in the gluten proteins even in the absence of mechanical treatments. The nature and extent of these changes has been addressed in a few studies (Bonomi and others 2004) that also related these features to flour strength (Bonomi and others 2006), and highlighted solvation-dependent exposure on the protein surface of previously buried hydrophobic sites (Iametti and others 2006; Mariotti and others 2008). Other spectroscopic studies addressed structural changes occurring in the absence of any mechanical deformation; for instance, by intimately mixing flour and ice at subzero temperatures and allowing the mixture to thaw (Peressini and others 2008).

In all cases, the solvated proteins become flexible enough to undergo further structural modifications upon mixing and kneading (see Figure 3.4). These modifications depend on the energy input and on the procedure and equipment used, as well as on the presence of components that may affect the properties of interacting species (for example, redox-active compounds, enzymes, shortenings, and so on) (Huschka and others 2012). Usually, mixing results in a rearrangement of the pattern of two major types of interactions: disulfide bridges and hydrophobic contacts between surface-exposed regions. The amount of water in dough and the water available for chemical reactions or yeast and microbial metabolism and growth reportedly also affect the leavening of various bakery products.
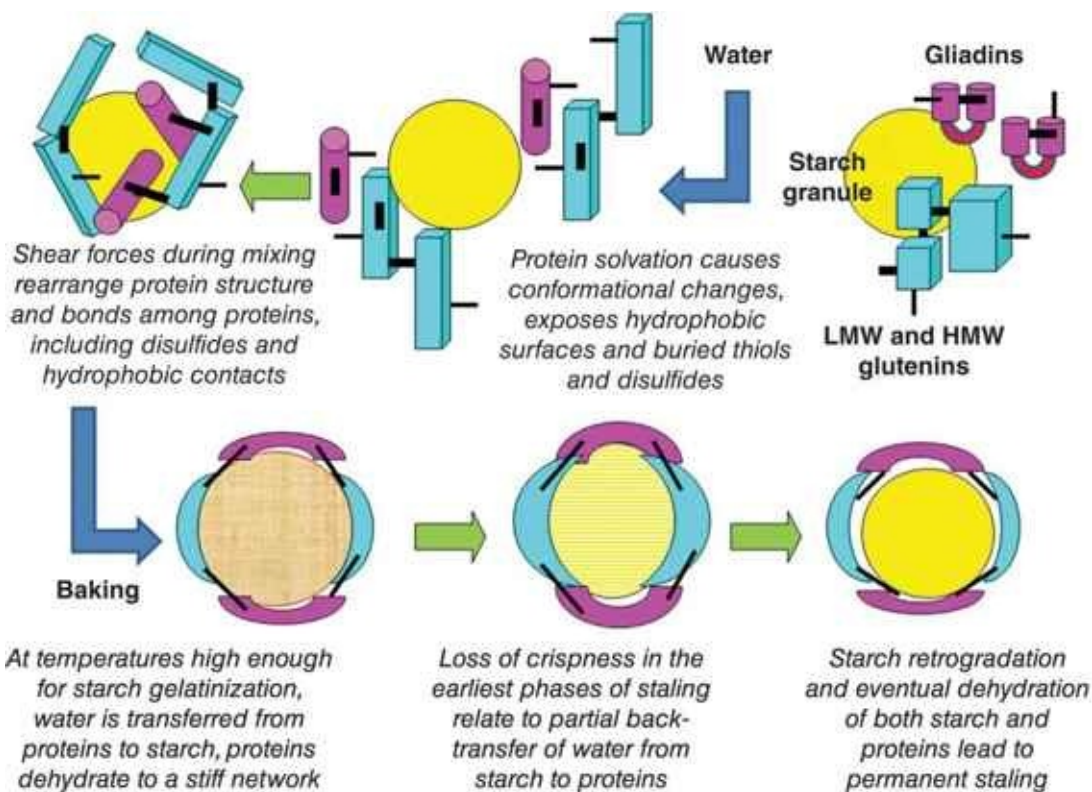
Figure 3.4 A schematic view of the main conformational changes and mass transfer events occurring in the preparation and storage of baked goods. Thin lines indicate thiols, thick lines indicate disulfide bonds.

During baking, protein-bound water and any residual free water present in the system are used for starch gelatinization (Figure 3.4) in a process that may be controlled by the presence of lipids and has a different time course than transfer from other water-containing polymeric systems, such as the non-cellulose, non-starch polysaccharides. In general, loss of water from the gluten network during baking is essential to some properties of the baked product, such as firmness and friability. Rates of water transfer between macromolecules should match those of other events occurring during baking, such as gas expansion and transient activation of enzymatic activities. Of course, the presence of water-retaining polymers other than proteins (most relevantly, non-starch polysaccharides) may have a profound impact on the kinetics of individual steps in these processes and affect to a variable extent the product properties, as do baking conditions and heat transfer issues in general.

After baking, water transfer events occur in reverse to those outlined earlier, with significant effects on the shelf-life of the products. In the earliest steps of storage, water is reversibly transferred from starch to the protein network, a process that may result in decreased crispness, and may be sensitive to atmospheric humidity in the absence of suitable precautions. In later steps, additional water molecules are transferred from starch to proteins in an almost irreversible process that is accompanied by starch retrogradation, leading to an increase in product crystallinity. Irreversible loss of water may eventually occur by evaporation on a longer timescale or when storage is inadequate. The "buffer" effects of the hemicellulosic components and the "barrier" effect of lipids may play a major role in determining the rate of water transfer of individual steps in all these events.

The status of water (free or bound) and the nature of the water-binding macromolecules is also of great relevance to the properties of frozen products, particularly products that are frozen before domestic or commercial baking. Here, assessing water content and distribution

could be of great interest, as could assessing the mobility of water in the system (Bonomi and others 2012).

Protein–protein interactions

Interaction within gluten proteins

Interprotein disulfides are by far the most abundant – if not the sole – covalent interaction of interest among different proteins prior to baking (at least when specific enzymes are not added, as discussed in a separate contribution). Whether non-covalent interactions are of significance before the addition of water is debatable, because these interactions cannot be assessed on proteins in the dry state.

The addition of water results in swelling of distinctive regions of individual gluten proteins, and mechanical deformation of the protein structure during mixing and kneading exposes hydrophobic side chains and cysteine residues (or disulfide bridges) that also may be inaccessible in the compact form in which proteins are stored and so cannot participate in the thiol–disulfide exchange that is essential to network formation. Indeed, thiol blocking reagents reportedly impair dough development. Accessibility of protein thiols to suitable reagents has also been introduced as a possible approach to evaluate compactness of the structure in a number of wheat-based products and materials (Mariotti and others 2011; Bonomi and others 2012).

Obtaining the highest number of interactions among proteins requires a fairly precise control of mechanical denaturation, as over-kneading weakens the interactions among proteins and the strength of the gluten network. This occurs as a consequence of the conversion of relatively rigid elements of secondary structure (for example alpha helices and beta-sheets) into various types of "random coil" structures that do not contribute to the strength of the overall gluten network. Several studies have relied on Fourier Transform Infrared spectroscopy (FTIR) to address the nature and extent of the structural changes occurring during mixing, often in correlation with rheological measurements, as done also through ligand-binding studies at various steps of mixing (Bonomi and others 2011). These approaches suggest re-formation of intraprotein interactions in a "stressed" dough, and indicate that various factors (including water availability and accessibility, as water competes with structure-stabilizing intraprotein and interprotein H-bonds) play a role in changes involving elements of the secondary structure. A coarse schematic representation of the various molecular modifications that may occur to proteins during these phases of the process is shown in Figure 3.4.

Leavening also influences the behavior of proteins, not only because of the modest mechanical stress associated with bubble formation, but also because of changes in the local pH and the appearance of a novel hydrophobic surface, that is, the gas inside the foam cell. The presence of an apolar surface may cause a rearrangement of some proteins, and pH changes due to microbial or yeast metabolism may affect the protonation of surface groups on proteins, and thus their ability to interact with water.

During baking, protein-bound water is transferred to starch in a process that depends kinetically on the temperature reached in any given point of the product. As already stated, other ingredients may affect these transfer events. The amount and type of added lipids are of paramount relevance here, as lipids at the interface between the water–protein system and

starch limit water migration. Note that simple monosaccharides and mono- or disaccharides (including sucrose, maltose, HFCS, and glucose) may modulate water availability, and the rate of water transfer to starch components.

During baking, the macroscopic phenomenon of bubble (foam) expansion may stretch the protein/starch film in individual foam cells until it is very thin. This aids interprotein interactions by increasing protein concentration, in particular as water previously involved in protein solvation is now either transferred to starch (in the product interior) or evaporated (from the product surface). The mutual equilibrium between these events relate in a promptly appreciable way to the physical and sensory features of the product, and may contribute significantly to the specific sensory and shelf-life characteristics of the product.

Interaction among wheat and non-wheat proteins in baked foods

No evidence has been brought forward – so far – of covalent interactions among wheat proteins and proteins from added sources. These can be represented by common ingredients in a broad variety of popular foods, as exemplified by milk or eggs, but may derive from uncommon sources, such as those encountered in bakery products containing grains other than wheat, or proteins from legumes.

Usually the proteins of non-wheat origin participate in their own network (Elkhalifa and others 2006) that forms in addition to the one formed by gluten proteins and using the same denaturation steps as those involving proteins of wheat origin. The most remarkable difference here is that most of the non-wheat proteins are added in a solvated and well-structured form. Only milk caseins are characterized by being intrinsically unstructured, due to the relative abundance of proline residues in their sequences. The non-wheat protein network intertwines with the one provided by gluten proteins, but it may replace the gluten network structure and may also act as a source of water for starch gelatinization in gluten-free products.

Non-wheat proteins are also of interest because of their ability to interact with lipids, as occurs for specific lipoproteins in egg yolk in their native state. In other cases (for instance, whey proteins) the emulsifying ability is maximized upon partial unfolding of their structure. In some specific products, non-wheat proteins are indeed mechanically unfolded to form or stabilize foams and emulsions prior to flour incorporation into the batter.

The addition of non-wheat flours, particularly untreated legume flours and/or non-heat-treated protein fractions, is often a source of enzymatic activities, as well as of non-protein components. Some of the enzymatic activities in these preparations may act on various gluten proteins by promoting the formation of additional interprotein bonds, either directly or through some reaction by-products.

Interactions with other components

Cellulose, hemicellulose, and other carbohydrates

The crystalline structure of cellulose makes it essentially impervious to water even at the temperatures reached in the outermost part of the product during cooking, so that its participation in water exchange events is minimal. However, the water-holding ability of all polysaccharides may be decreased when their size is decreased (for instance, by using

suitable hydrolytic enzymes). Use of cellulolytic-type enzymes in flour ameliorants is common, because they contain a number of additional enzymatic activities (typically: xylanases, rhamnosidases, alpha-glycosidases, and other hydrolytic enzymes acting on pentose-based polymers).

These activities act on linear and branched regions of the complex mixture of polysaccharides that form the hemicellulosic fractions in flour. The physicochemical properties of these polysaccharides, including solubility and their ability to retain water, depend on the size of the molecule (the smaller the molecules, the higher their solubility and their ability to retain water), on its structure (branched structures favor solvation), and on the chemical modifications of the sugars in the structure. Small hemicellulosic polymers constitute the soluble portion of the fiber in cereal-based products. Both the soluble and insoluble fractions have received much attention by nutritionists due to their role in human physiology and to their interactions with intestinal microbial flora.

Lipids and lipid-related components

Lipids are present in wheat flour at much lower levels than starch or protein, but they are relevant to the functional properties of other polymers in bread making. They may be endogenous to flour or, most commonly, come from added shortening and/or surfactants. They interact with starch and gluten proteins and have a role in foam cell stabilization, which affects bread loaf volume, crumb structure, and crumb firming (Paryet and others 2011).

As stated earlier, lipids may interact with other components of dough and batters either through a "coating effect" or through more specific molecular interactions. A generic "coating effect" has been proposed in modulating water exchange events in various steps of baking, including staling. Binding or complexing of lipid by flour proteins during dough development may involve lipid mesophase transformation and the non-specific occlusion of lipid phases within the gluten network (Carr and others1992) or on the surface of gluten proteins (Huschka and others 2012). Lipids (and other ligands) may also form inclusion complexes with amylose, in a process requiring a conformational change involving the transformation of amylose double helices to a single helix (a so called V-amylose). This compact structure is thought to have a central hydrophobic cavity hosting the hydrocarbon chains, and the complexed lipids behave differently from free ones (Putseys and others 2010).

Added emulsifier in some shortening formulations (or monoglycerides and diglycerides derived from added lipolytic activities present in enzymatic improvers) may alter the effects of lipid addition by modulating their interaction with either starch or proteins, and their structure in general. Among the affected traits in baked goods are volume, oven-rise, crust color, crumb texture and color, shelf-life, flavor, and aroma. Esters of monoglycerides have been proven to significantly increase bread oven-rise and specific volume (Moayedallaie and others 2010). The detailed mechanisms of these effects, however, are still being investigated.

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4
Rye

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Introduction

Rye (*Secale cereale* L.) is a traditional raw material used for baking in Northern and Eastern Europe. The flavor and structure of rye bread are quite different from those of wheat bread, and vary depending on flour type, other raw materials and ingredients, process, baking conditions, and time, as well as on the size and shape of the bread. Generally consumed as whole grain products, rye offers a good source of dietary fiber, phenolic compounds, vitamins, trace elements and minerals. Rye bread has also been shown to have beneficial physiological effects especially with respect to glucose metabolism and satiating effects. Expanding research data strengthen the position of rye grain as an important raw material for healthy foods, and the potential for developing novel products is growing with the knowledge about its transformations during milling and baking processes.

Production and consumption

In terms of total production, rye is a minor cereal. Only about 0.7% of the total cereal grain crop is rye (FAO 2007). The present world harvest of rye is about 14.8 million tons, most of which is produced in the northern part of the region from the Nordic Sea to the Ural Mountains. Because rye is extremely winter hardy and can grow in sandy soils with low fertility, it can be cultivated in areas that are generally not suitable for other cereal crops. Major producers of rye are Russian Federation, Poland, Germany, Belarus, and Ukraine. In 2006, 80% of the world's rye production was in these five countries (Sahlström and Knutsen 2010). Food and feed uses of rye are at the same level, and make up the majority of rye uses (Table 4.1)

Table 4.1 Uses of rye grain (FAOSTAT 2007. Reproduced with permission of FAO.)

Type of use	Million tonnes	%
Feed	6467	43,6
Food	5531	37,4
Seed	1549	10,5
Processing	743	5,0
Other	661	4,5

Over one-third of the total rye crop is used for food, predominantly for various types of bread. Rye consumption in the "Rye Belt" countries is in the range of 10–30 kg per person per year (Sahlström and Knutsen 2010).

The rye grain

The basic composition of the rye grain is similar to that of wheat (Table 4.2). Compared to wheat, rye generally contains less starch and crude protein but more dietary fiber (DF). The DF content of rye is actually the highest among the common cereals. The major DF constituents of rye are arabinoxylan (AX), β-glucan, cellulose, fructan, and lignin (Åman and others 2010). Rye contains more fructan, mixed-linked β-glucan, and AX but similar amounts of cellulose and Klason lignin as compared to wheat (Nilsson and others 1997a). The range of dietary fiber content in different rye varieties in the EU-Healthgrain project variety screen was 20.4–25.2% (Nyström and others 2008). The DF in cereal grains is located mainly in the outer layers of the kernel, especially in the bran. Wheat and rye have a similar bran content, but rye contains more cells within the endosperm, and thus has a higher DF content (Nyman and others 1984; Åman and others 1997).

Table 4.2 Chemical composition of rye (% of dry matter)

Component	Rye	Wheat 100[a]	Wheat 66[b]
Ash	2	2	0.5
Fat	2–3	3	1
Protein	10–15	12–14	13
Starch	55–65	67–70	84
Dietary Fibre	19–22	13–17	3
Arabinoxylans	8–10	6	
β-Glucan	2–3	0.8	
Cellulose	1–3	2.5	
Lignin	1–2	0.8	
Fructan	4–6	1.4–2.6	

(Nyman and others 1984; Andersson, and others 1992; Clydesdale 1994; Härkönen and others 1997; Åman and others 1997, 2010; Boskov-Hansen and others 2003; Fretzdorff and Welge, 2003; Karppinen and others 2003.)

[a]Extraction rate 100 = whole grain flour

[b]Extraction rate 66 = 66% of grain is milled in this flour. This extraction rate corresponds to white wheat flour.

The distribution of rye proteins in the Osborne solubility classes indicates that in comparison to wheat, rye contains less glutelins. Rye prolamins, or secalins, are not considered to play a role in rye baking either because of their low concentration or their interactions with other components (Shewry and Bechtel 2001). Rye starch is similar in its structure and properties to starches from wheat and other cereals. It consists of two types of polymers, amylose and amylopectin, with amylose accounting for 24–26% of total (Shewry and Bechtel 2001).

The size of rye grains differs between varieties. Hybrid varieties commonly have larger grains than population varieties. The main morphological characteristics are similar to other grains. A review on the microstructure of developing and mature rye grain has been made by Simmonds and Campbell (1976). The microstructure of transversely sectioned mature rye

grain is shown in [Figure 4.1](#). The four morphologically different tissues of the grain are the layers of pericarp and seed coat, embryo, aleurone, and starchy endosperm. The embryo is located on the dorsal side of the grain. The pericarp consists of lignified, dead cell layers. The aleurone cells form the outermost layer of the endosperm and represent live tissue at maturity. The aleurone layer of rye is typically only one cell layer thick. Pericarp, seed coat, and aleurone layer are the main parts of the bran fraction produced during milling. Similarly to wheat and barley, rye contains two types of starch granules: large lenticular A-granules (15–25 μm in diameter) and smaller polygonal B-granules (<10 μm in diameter).
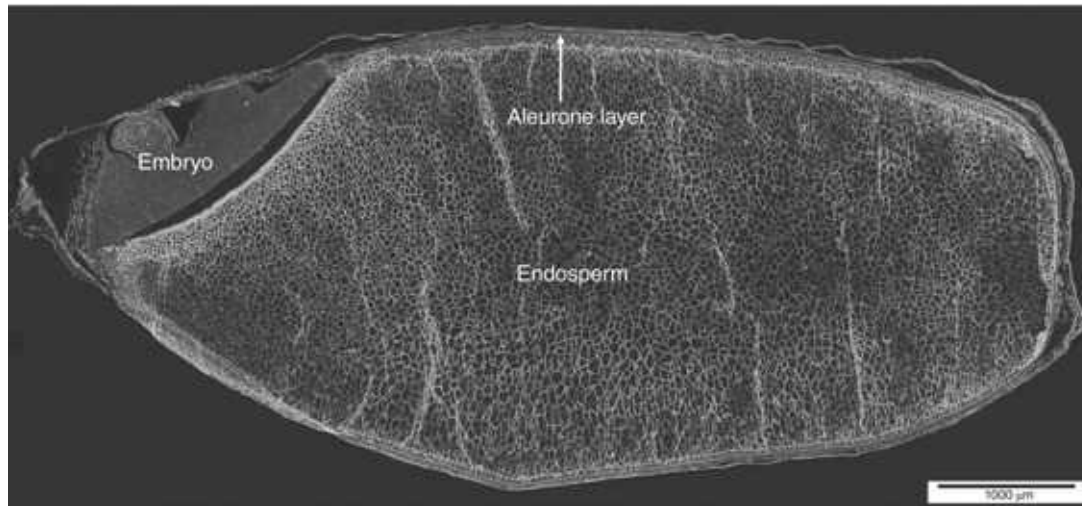
Figure 4.1 The microstructure of rye grain.

The starchy endosperm constitutes about 80–85% of the weight of the whole kernel, the embryo 2–3%, and the outer layers about 10–15%. The embryo is located at the basal end of the grain. The cells of the embryo have thin walls and contain a large nucleus. They also contain protein bodies and fat globules called spherosomes. The germ is composed of two functionally different parts: the embryo proper and the scutellum, which is a shield-like structure appressed to the endosperm. At germination, the scutellum becomes a digesting and absorbing organ that transfers the stored nutrients from the endosperm to the growing parts of the embryonic axis.

Arabinoxylans

Arabinoxylan is the major dietary fiber component of rye grain, and contributes remarkably to the water binding properties of the flour. The average arabinoxylan content in a set of 18 Swedish rye grain samples was 8.6% (Andersson and others 2009). The total arabinoxylan contents in European rye grains varied between 12.1–14.8% in the bran and 3.1–4.3% in flour (Nyström and others 2008). The chemistry and solubility of the arabinoxylans is different in different parts of the grain. The ratio of soluble to total arabinoxylans is 71% in the endosperm, 25% in the aleurone, and 14% in the outer bran (Glitsø and others 1995). Furthermore, the ratio of arabinose to xylose (Ara/Xyl) differs in different parts of the grain being 0.40 in the aleurone, 0.75 in the endosperm, and 0.63 in whole rye. Ferulic acid is esterified to arabinoxylans in rye cell walls (Vinkx and others 1991).

The arabinoxylans are divided on the basis of solubility into water-extractable (WE) and water-unextractable pentosans (WUE). The WE arabinoxylans are extractable with cold water, whereas WUE pentosans are alkali soluble. The percentage of soluble arabinoxylans is higher in the endosperm than in the bran and shorts fractions (Delcour and others 1989).

Rye arabinoxylans have been classified on the basis of extractability: Arabinoxylan I has an Ara/Xyl ratio of 0.5 and it is totally water extractable, Arabinoxylan II has a Ara/Xyl ratio of 1.4 and it is partly water-extractable (Bengtsson and Åman 1990). Rye NSP showed significantly higher viscosity in 0.1 M NaCl than in 0.01 M NaCl solution (Girhammar 1992). Compared with the intrinsic viscosity of other polysaccharides, the arabinoxylans show a similar value to guar gum (2.3–6.8 dl/g), but are more viscous than dextran (0.214 dl/g) and gum arabic (0.12–0.25 dl/g) (Mitchell 1979). Rye varieties differ in terms of chemical structure and viscosity of arabinoxylans. Viscosity measurement showed that Arabinoxylan I fractions from two cultivars were different due to different proportions of high molecular size polymers (Nilsson and others 2000).

Bioactive compounds

In addition to macronutrients and DF, grains contain a wide range of micronutrients and bioactive compounds. In rye, as well as in other cereals, bioactive compounds are concentrated in the germ and the outer layers of the kernel, which are also richest in DF (Nilsson and others 1997b; Glitsø and Bach Knudsen 1999; Liukkonen and others 2003). The main bioactive compounds in rye are lignans, phenolic acids, alk(en)ylresorcinols, phytosterols, trace elements and minerals, folates, tocopherols and tocotrienols and other vitamins. Table 4.3 shows concentrations of some major bioactive compounds in rye.

Table 4.3 Concentration of the major bioactive compounds in rye (µg/g)

Compound	Amount	Reference
Lignans	19–22	Penalvo et al 2005, Smeds et al 2007
Phenolic acids	1117–1244	Shewry et al 2010
Alk(en)ylresorcinols	901–1030	Shewry et al 2010
Folates	865–1018	Shewry et al 2010
Tocopherols and tocotrienols	56–59	Shewry et al 2010
Plant sterols	1110–1233	Shewry et al 2010

The phenolic compounds in rye grain, as well as their processed-induced changes and bioavailability and suggested bioactivities have been reviewed by Bondia-Pons and others 2009. The phenolic compounds are concentrated in the outer layers of the grain. Phenolic acids, whereof ferulic acid the most abundant, are at the highest concentration of the phenlic compounds in rye (Table 4.3). Most of the phenolic acids are present in the grain and flour in bound form, f.ex. ferulic acid is esterified to arabinoxylan. A portion of the ferulic acid in the cell wall is present as dehydrodimers (Faulds and Williamson 1999). The potential health benefits of phenolic acids are suggested to relate to their antioxidant activity.

It was long assumed that matairesinol and secoisolariciresinol are the main plant lignans also in rye grain. Now it is known that pinoresinol, syringaresinol, lariciresinol and isolariciresinol comprise over 80% of the total lignan content of rye (Heinonen and others 2001). Very recently also polymeric rye lignans have been detected (Hanhineva and others 2011). Many of the lignans are converted by the intestinal microflora to the mammalian lignans enterodiol and enterolactone, which have been linked with various positive health effects.

Alk(en)ylresorcinols have received particular interest as potential biomarkers of the intake of wholegrain rye and wheat products (Ross 2012). They occur in rye as three major homologs: C17:0 ($\approx$ 24%), C19:0 ($\approx$ 32%) and C21:0 ($\approx$ 24%) (Ross and others 2003). Alkylresorcinols have been linked to certain bioactivties, and have also been found to be incorporated into human erythrocyte membranes.

Sitosterol is the main sterol in rye ($\approx$ 50%) and other cereals (Piironen and others 2002, Shewry and others 2010). The other sterols in rye in decreasing order are campesterol, sitostanol, campestanol and sigmasterol. Six folate vitamers occur in rye. Formylfolates (5-HCO-H4-folate, 10-HCO-H2-folate and 10-HCO-folic acid) and 5-CH3H4-folate are the most abundant vitamers in rye flour. The R-tocotrienol (38%) and R-tocopherol (32%) are the

major forms of tocols. The average proportion of tocotrienols in the Healthgrain variety screen was 59.6% of the total tocols (Nyström and others 2008).

Processing may influence the level and bioavailability of the bioactive compounds in cereal. However, knowledge on influence of processing on levels of bioactive compounds is scarce. Levels of folate and easily extractable phenolic compounds have been found to increase during germination and sourdough baking of rye (Liukkonen and others 2003a; Kariluoto and others 2003), whereas levels of phytate (Frölich and others 1986; Larsson and Sandberg 1991), alkylresorcinols (Verdeal and Lorenz 1977) and tocopherols and tocotrienols (Piironen and others 1987; Liukkonen and others 2003a) have been reported to be reduced in sourdough baking process. In our recent study (Liukkonen and others 2003b), the folates were shown to be sensitive to heat processing (extrusion, autoclaving, puffing, roasting). However, the folate concentration of germinated and subsequently heat prosessed rye grains was still remarkably higher than that of native grains. The amounts of plant sterols and lignans changed very little during the heat processing. The amounts of tocopherols and tocotrienols and alk(en)ylresorcinols decreased during the extrusion but remained almost unchanged during other heat processes. In conclusion, it was proposed that many of the bioactive compounds in whole grain rye are stable during food processing, and their levels can even be increased with suitable processing.

Nutrition and health-effects

Dietary guidelines recommend increasing the intake of whole-grain cereals, but this is still below the recommendations. Consumed as whole grain products rye is an important source of DF, trace minerals, and certain vitamins. In addition whole grain rye products contain phytochemicals that together with vitamins, minerals and DF may have role in disease prevention. In Finland, about 40% of daily DF intake comes from rye. From 150 g of whole grain rye bread it is possible to obtain 40–60%, 22%, 17%, 32–40%, and 43% of the recommended daily intake of DF, folates, magnesium, and zinc, respectively.

An increasing amount of research data indicates that rye bread has beneficial physiological effects. Compared with white wheat bread, whole-meal rye bread has been shown to reduce the need for postprandial insulin and to improve first-phase insulin secretion – both factors associated with the effective regulation of glucose metabolism and a reduced risk of type 2 diabetes (Leinonen and others 1999; Juntunen and others 2002, 2003a, 2003b) – as well as cause changes in adipose tissue gene function (Kallio and others 2007). Rye product consumption has been linked with increased feelings of satiety (Isaksson and others 2012), and recent metabolomic data also suggest changes favorable for weight maintenance (Lankinen and others 2012).

Rye bread has been shown to improve bowel function (Gråsten and others 2000; McIntosh and others 2003), contribute to the growth of bifidobacterium, reduce the concentrations of some compounds that are putative colon cancer risk markers (Gråsten and others 2000), and increase the serum concentrations of enterolactone (Juntunen and others 2000). In epidemiological studies, a high enterlactone concentration has been related to a reduced risk of acute coronary events (Vanharanta and others 1999) and breast cancer (Ingram and others 1997; Pietinen and others 2001).

Consumption of rye products has also been related to possible colon and prostate cancer risk-reducing effects (Korpela, and others 1992; Landström, and others 1998; Davies and others 1999; Bylund and others 2000; Gråsten, and others 2000; Mutanen, and others 2000). In the Finnish study by Pietinen and others (1996), a reduced risk of death from cardiovascular diseases was related to the consumption of rye products.

The rye results are consistent with the health claim that the US Food and Drug Administration authorized in 1999 for foods that contain 51% or more whole-grain ingredients. According to the health claim, "Diets rich in whole-grain foods and low in total fat and saturated cholesterol may reduce the risk of heart disease and certain cancers". It is stated that in addition to dietary fiber, whole-grain foods contain abundant amounts of antioxidant vitamins and phytochemicals that seem to act together to provide protective effects. In Europe, the European Food Safety Authority (EFSA) has recently accepted a health claim about the consumption of rye fiber and changes in bowel function (EFSA, 2011).

Consumption as food

As already stated above, rye is, in contrast to wheat, a special grain, because it is mostly consumed as whole grain flour in breads and other cereal products. Examples of products commercially available to consumers and their ingredients are shown in Table 4.4.

Table 4.4 Rye-based consumer products

Milling products	Bread products	Other rye products
Whole grain rye	Rye bread	Rye porridge
Steel cut rye	Crispbread	Berry pastries
Crushed rye grains	Thin crispbread	Karelian patries
Malted and crushed rye grains	Rye rolls and buns	"Kalakukko" – rye-dough-covered baked fish containing fish, meat and /or vegetables
Precooked rye kernels	Rolls, buns and breads containing wheat/rye-mixture	"Mämmi" – Finnish Easter pudding
Malted rye kernels	Parbaked rye product	Rye pasta
Whole grain rye flour		Rice-rye-mixture
Shifted rye flour (variations is ash content)		Snack products
Rye bran		Crispbread sandwich
Rye flakes		Rye hamburger
Four-grain flakes with rye		
Toasted rye flakes		
Breakfast cereals (muesli, others)		
Sourdough rye bred mix		

Milling products

Although grains have been used whole in various ways as human food, usually they have been ground in preparation for cooking. Most rye for bread making is milled by a roller milling procedure resembling that used for wheat milling. Grinding changes the mechanical properties of the various tissues of the grain. Pericarp, seed coat, and aleurone layer are the main parts of bran fraction produced during milling. The miller separates the bran and the embryo from starchy endosperm to produce a high yield of flour. The toughness of the bran

enables it largely to withstand the crushing and tearing that is required to detach the endosperm from the bran.

Milling can also be used to enrich different grain tissues, for example pericarp/testa, aleurone, and endosperm. Milling rye in a roller mill produces as many as 50 different mill streams varying in yield percentage, gross chemical composition, and technological properties. For example, the viscosity and dietary fiber characteristics are important for the technological and nutritional properties (Glitsø and Bach Knudsen1999). Analogously to wheat bran, rye bran is a commercial milling product containing the outer layers of the grain but more endosperm than wheat bran. The dietary fiber content in 8 Nordic rye bran products varied from 41 to 48% of dry matter, starch content from 13 to 28%, and protein content from 14 to 18% (Kamal-Eldin and others 2009).

Bread products: rye bread technology

Baking with rye is different from baking with wheat in many respects. The main difference between rye and wheat flours is that rye protein cannot form a continuous network and an elastic dough. Instead rye pentosans (mainly arabinoxylans) are able to bind water during mixing to produce a dough that can be baked into bread.

The most typical rye bread in Finland, Denmark, Russia, and the Baltic countries is *soft whole grain rye bread* made by using a sourdough method. In this method, the main ingredients – whole grain rye flour, water, and starter culture (usually seed from a previous sourdough batch with stable microflora) – are mixed and fermented for about 8–18 h. During the fermentation period the lactic acid bacteria and the sourdough yeast grow, and due to the microbial activity and the enzymatic reactions of the microflora, flavor compounds and flavor precursors such as amino acids are formed. The main components formed are lactic acid and acetic acid. After fermentation, more flour, water, and other ingredients are mixed with the sourdough to make a dough. The dough is left to rise for a short period, after which the breads are shaped, left to rise again, and baked.

Without sourdough, whole meal rye or wheat-rye flour mixes are very difficult to process because the acids and enzymes formed or activated during fermentation modify the protein and pentosan phases with positive effects on moisture, porosity, and crumb elasticity. Sourdough also provides an aromatic and pleasing flavor, and improves overall quality and shelf-life. The positive influence of sours are based on the increased swelling power of the pentosans and mucilages of rye flour and a simultaneous inactivation of some enzymes, particularly amylase (Brummer and Lorenz 2003).

Whole meal rye doughs contain high amounts of flour particles that have a high concentration of cell walls. The cell wall material is largely responsible for the water-binding capacity and rheological properties of rye doughs. The structure of the cell walls and, for example, the effects of preharvest sprouting on the composition of the grain play an important role in determining the baking quality of rye. Differences in rye raw material and technological operations cause structural alterations to the dough components. Hydration and degradation of cell walls have been found to have a noticeable effect on dough rheology and change the baking behavior of the dough and influence the structure of the bread (Fabritius and others 1997; Autio and others 1998). The sourdough process is commonly used in rye bread baking, and the acid conditions greatly affect enzyme activities and starch

gelatinization. Both the cell wall degrading enzymes and α-amylase affect the baking properties of rye doughs and the quality of breads. Dough softening during fermentation has been shown to be partly dependent on the swelling or fragmentation of cell walls induced by xylanase, whereas during baking this softening is mainly due to α-amylase.

The most important methods for determining the baking quality of rye flour are the falling number and the amylogram, which are both related to α-amylase activity. Rye flour with a low falling number gives soft, sticky dough and the resulting bread is dough-like. Rye flour with a high falling number yields rigid stable dough but the resulting bread is dense and hard.

Another popular type of rye bread is *crispbread*, which has a long shelf-life due to its very low water content. For the production of crispbread, rye with a low amylase activity is required. There are three types of rye crispbread: normal yeast fermented, sourdough fermented, and cold crispbread, which is baked without the addition of yeast. Crispbread has a long shelf-life due to its very low water content (5–7%).

Third type of rye bread is *pumpernickel*, which originates from Germany. It is produced from whole meal rye flour with the sourdough process. Crispbread is now produced in different countries using many different recipes and baking conditions. The baking temperature is kept rather low (100–170 °C), and baking time ranges from 10 to 36 h. Pumpernickel bread has a very dark and dense crumb, highly aromatic, bittersweet taste, and very long shelf-life. The bittersweet taste of pumpernickel is due to the acids that are formed in the sour fermentation and the amylolysis of the starch during sourdough fermentation, proofing, and baking that produces glucose, maltose, and dextrins (Pyler 1988; Seibel and Weipert 2001).

Other rye products

In addition to breads and different types of flours, there are many other uses for rye as food. Rye porridge is traditionally made of rye flour, but nowadays rye flakes are used for making porridge. "Mämmi", the Finnish Easter pudding, is made of rye malt flour, sugar, and spices. Different types of pies and pastries originate from Karelia on the border of Finland and Russia. A traditional Karelian pastry is made with a very thin coating containing rye and wheat flour. The filling is made of cooked mashed potatoes, rice or barley pudding. New products include the blend of white rice and precooked rye grains for use as an accompaniment, pasta products that contain both wheat and rye, instant rye flakes mixed with dry berries for breakfast use, and snack products.

Flavor of rye grain

The characteristic intense flavor of rye products is formed through the flavor components and precursors of rye, but particularly through the processing techniques used.

Chemical compounds influencing rye flavor

Volatile compounds may influence the perceived flavor of rye, the dominant compounds being aldehydes, ketones, and alcohols (Schieberle and Grosch 1994; Hansen 1995; Grosch and Schieberle 1997; Kirchhoff and Schieberle 2002; Pozo-Bayón and others 2006). Non-volatile compounds may influence flavor directly, or indirectly as flavor precursors through reactions that form new flavor compounds. *Phenolic compounds* contributing the flavor are alkyl(en)resorcinols, lignans, and phenolic acids (mainly ferulic acid, but also sinapic, *p*-coumaric, and caffeic acids) (Andreasen and others 2000a, 2000b; Heiniö and others 2008). Heat or microorganisms may decompose the phenolic acids into compounds with an intense flavor; for example ferulic acid is a source of 2-methyl-4-vinylphenol, described as having a burnt, tar-like flavor (Hansen 1995). At high temperatures, free *amino acids* or small peptides and free *sugars* are important flavor precursors that form volatile compounds in the Maillard reaction that affect flavor, such as pyrazines, pyrroles, and furfurals, which often give a roasted note. In addition, *lipids* influence the flavor, either as hydroxy fatty acids resulting from the oxidation of lipids, or as free fatty acids resulting from the lipase-catalyzed hydrolytic oxidation of lipids. All chemical compounds are not flavor-active; however, the perception depends on the odor and flavor thresholds and the relative amounts of compounds in the product.

Flavor of native rye

The chemical composition of native rye grains varies significantly depending on the environment, the genotype, and their interactions. The components of the soil influence the amino acid, lipid, and sugar composition of the grain, which also indirectly influences the perceived flavor. Thus, the effect of the season and the cultivation area might be more dominant for flavor formation than, for example, the rye cultivar. For example, the nitrogen content of the soil greatly influences the composition of amino acids, and thus the protein composition of the grain. The season is a dominant factor, especially for protein and fat production. Different grain varieties have their characteristic flavor; for example, the oat-like flavor is milder than the rye-like flavor.

The flavor of native rye is relatively mild when compared to the flavor of processed rye (Heiniö and others 2003b). In mechanical milling fractionation, the rye kernel is separated into endosperm, shorts, and bran fractions, each having a characteristic flavor. Between the very mild tasting innermost endosperm of the grain and the strong and bitter tasting bran, a rye-flavored fraction without bitterness has been observed (Heiniö and others 2003a). The phytochemicals are mainly concentrated in the germ and bran fraction of the kernel (Shewry and Bechtel 2001; Decker and others 2002), but the middle fraction also contains significant amounts of bioactive compounds (Liukkonen and others 2003a, 2003b). One reason for the bitter taste of rye was found to be the small molecular weight peptides, as shown by using

different hydrolytic enzymes (Heiniö and others 2012). Enzymes could possibly also be used to decrease the perceived bitterness.

Flavor formation in processing of rye

The grain flavor is considerably modified by several processing techniques, such as germination and subsequent drying, extrusion cooking, autoclave, puffing and roasting techniques, or microwave heating, which all have a high processing temperature in common. In general, some kind of processing is required for fine-tuning the rye flavor and for achieving different types of rye products (Hansen 1995; Schieberle 1996; Grosch and Schieberle 1997; Heiniö 2003; Heiniö and others 2003b).

Sourdough fermentation used in baking rye bread is perceived as being intense and bitter in flavor (Hellemann and others 1987, 1988; Heiniö *et al.* 1997). Fermentation strengthens the sour, rye-like flavor, and influences mainly the bread crumb flavor, whereas baking results in a roasted flavor. For consumers, the most dominant sensory attribute of rye bread is its rye-like flavor, but perceptions of sourness and saltiness (which have been shown to compensate each other) are substantially associated with rye bread (Hellemann and others 1988; Heiniö and others 1997). Salt-free bread has a bland taste, and salt is used in foods for improving the taste, texture, and stability, and for strengthening the flavor. The perceived sourness of rye bread is shown to be strongly associated with the concentration of lactic and acetic acids (Hellemann and others 1988).

The oxidation of lipids and enzymatic and heating reactions are the key reactions influencing flavor formation in rye bread (Schieberle 1996). Volatile compounds evaporate from flour due to oxidation reactions. Enzymatic reactions produce flavor-active compounds during sourdough fermentation and at the beginning of baking. The enzymes may originate from the flour, from the yeast or lactic acid bacteria, or from the additives. The flavor compounds produced during the baking process are possibly the most essential compounds for the flavor of rye bread, and they mainly form during the heat treatments, such as the Maillard reaction and caramelization.

Germination is halted by a heat treatment, and is thus very effective in modifying the cereal flavor, resulting in a fresh, cereal-like, somewhat roasted flavor and hard, crispy texture to rye (Heiniö and others 2003b). Germinated grains are also a good source of free amino acids and sugars, which act as flavor precursors.

Summary

In terms of total production (less than 1% of world production) rye is a minor cereal. The world rye production largely takes place in the Northern part of the region from the Nordic Sea to the Ural Mountains. In countries with a high consumption of rye, the per capita consumption is in the range of 10–30.

In contrast to wheat, rye is mostly consumed as whole grain flour in breads and other cereal products, which makes rye products a good source of DF and micronutrients and bioactive compounds such as phenolic compounds, vitamins, trace elements, and minerals.

Rye proteins, unlike wheat protein, cannot form a continuous network and an elastic dough. Rye pentosans (mainly arabinoxylans), however, are able to bind water during mixing to produce a dough that can be baked into bread. The flavor and structure of rye bread are also quite different from those of wheat bread, and they vary depending on flour type, other raw materials and ingredients, process, baking conditions, and time, as well as the size and shape of the bread.

There has been much research data about the health effects of rye in recent years, supporting the bioavailability of many of the phytochemicals, and demonstrating the favorable effects on glucose metabolism and the satiating effects of rye bread, as well as its protective effects against certain cancers. There is thus a good reason to work for an increased use of whole meal rye flour in various bakery products as well as in mixed-flour products. This demands that processing is developed that takes into account the sensory demands of the modern consumer.

Acknowledgments

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5
Rice

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Introduction

Rice (*Oryza sativa* L.) has been, throughout history, one of the most important foods in the human diet. Even today, rice grains sustain two-thirds of the world's population, although their contribution is different in the developing and developed countries. For instance, rice is the staple food for the Chinese and also for 65% of the total population in India. Rice is primarily consumed as milled rice, but there are also a number of products where rice is added as an ingredient, conferring creaminess, crunchiness, and firmness. Moreover, rice-based products have been the solution for consumers with allergenic problems. In this chapter the following aspects will be considered: a brief description of rice production, its physicochemical characteristics, modification of the nutritional properties of rice with processing, rice flour characteristics, rice breads, mixed flour breads, and other baked rice goods.

Production and consumption of rice

Rice accounts for 28% of the total cereal production, compared to wheat and corn production (Figure 5.1). Its importance as a food cereal in the human diet is slightly less than wheat, however, although this assessment is reversed when only the developing countries are taken into account. Rice cultivation is concentrated in the developing countries.
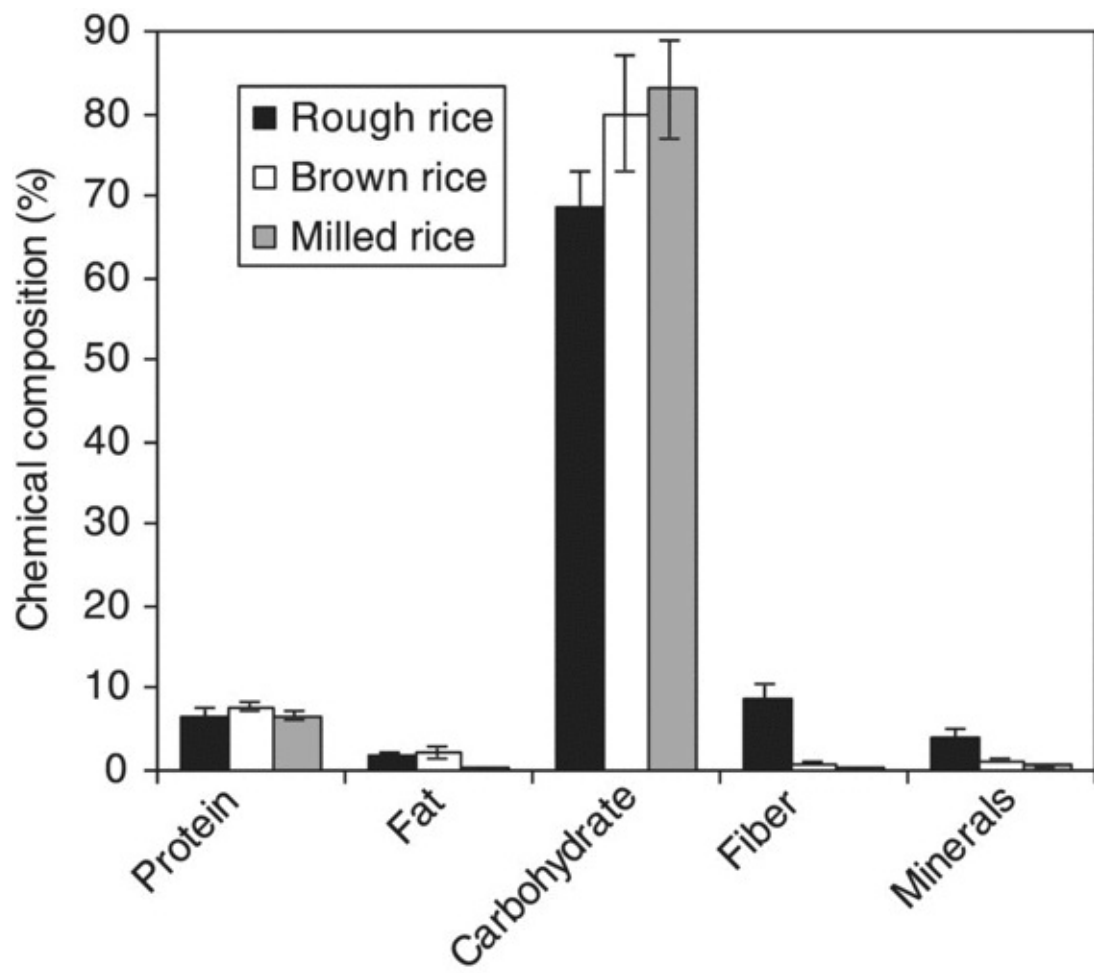
Figure 5.1 Range of mean content of the rice grain and its milling fraction at 14% moisture. (Data from FAOSTAT 2012.)

Rice is grown mainly in Asia, where 91% of the total world production is located (FAOSTAT 2012). China is the world's largest rice producer (29%) (Table 5.1), followed by India (22%), Indonesia (9%), and Bangladesh (7%). Rice cultivation is the principal activity and main source of income in those countries, and also the core of their food intake, sustaining those on very low incomes in many of Asian countries. The amount of rice and rice-based products available for human consumption in the different countries almost parallels rice production. With minor exceptions, practically all the rice produced in a particular country is also consumed there. The highest rice consumption is observed in China, although the trend drastically changes when the values are expressed as kilograms of rice consumed per capita and per year. In this way, rice consumers are mainly located in Vietnam, followed by Lao People's Democratic Republic, Bangladesh, Myanmar, and Cambodia. This is in contrast to rice consumption in the United States of America, where it is 12.4 kg per capita per year. This value is close to the average consumption of rice in the developed countries (13.0 kg per capita per year), compared to the 93.9 kg per capita per year of rice consumed in the

developing countries, which are also low-income countries.

Table 5.1 Rice production and consumption by countries

Countries	Rice (paddy equivalent)		
	Production (metric tonnes)	Human consumption (metric tonnes)	Human consumption (kg per capita per year)
China	187 397 460	153 883 545	115.1
India	144 570 000	123 841 478	106.3
Indonesia	57 157 400	42 197 952	187.8
Bangladesh	43 181 000	37 776 256	239.5
Viet Nam	35 942 700	21 372 599	248.2
Thailand	32 099 400	10 351 616	154.6
Myanmar	31 451 000	11 559 264	235.3
Philippines	16 240 200	17 196 862	193.8
Brazil	11 060 700	9 473 520	49.8
Japan	10 893 000	10 816 985	84.9
United States of America	8 998 730	3 823 760	12.4
Pakistan	8 345 100	3 757 817	21.7
Egypt	6 876 830	4 438 104	55.4
Cambodia	6 727 000	3 268 849	228.2
Republic of Korea	6 038 000	5 459 812	113.8
Nepal	3 680 840	3 309 390	117.0

Rice flour production

Rice is harvested and threshed to produce so-called paddy rice or rough rice, where the kernel is still within the hull or husk. Prior to consumption, rice must be milled which involves removing the husk, stripping the bran off of the endosperm, and finally eliminating broken and altered kernels. Rice mmilling is a sophisticated process when it is performed in the developed countries. Initially the paddy rice is cleaned through coarse screens to remove all the straw, stones, and other foreign objects that are larger than the rice kernels. The same process is repeated using fine screens to remove small weed seed, sand, stones, and other objects smaller than the rice kernels. Stones are separated from the rice product by density using specific gravity tables. After the cleaning step, the husk is removed by passing the rice through two rubber rolls that spin at different speeds. Brown rice obtained after dehulling and may be eaten as it is or milled into white rice. Milled rice, milled white rice, polished rice or polished white rice is obtained after removing the bran and germ from the brown rice. The many machines and methods designed for milling rice often use an abrasive system followed by frictional and polishing systems . Rice milling can yield from 4 to 40% broken kernels depending on the incoming rice quality and the milling equipment. Broken kernels are removed from the whole kernels through indent graders to obtain high quality table rice. Broken kernels can be further separated into various sizes according to their final use (brewing, screening, flour milling). In flour milling, broken kernels are subjected to different size reduction processes that take into account kernel hardness, which – regardless of the grinding method – governs kernel rupture and particle size (Chen and others 2004). In general, wet grinding, semidry grinding, and dry grinding are used to grind rice into flour (Yen 2004). Wet grinding has five main steps: soaking the broken kernels in water, grinding in excess of water to reduce the amount of damaged starch, filtering, drying, and sieving. This product is used in the production of different Asian specialities such as Japanese cake, Taiwanese cake, Indian fermented foods, and so on. This process is the most traditional for obtaining rice flour, but costs associated with this process are high due to flour loss, water consumption, treatment of wastewater, and high energy consumption. Semidry grinding slightly simplifies the previous method, by using three steps to grind the kernel. It involves soaking, drying to remove the excess of water (15–17% wet basis), and grinding (Yen 2004). The semidry flour has similar applications to the wet rice flour. However, this method is time consuming and costly due to the time needed for adjusting the moisture content of the kernels, the excessive consumption of energy during drying, water consumption, and the treatment of waste water. Dry grinding is also possible; in this case broken kernels are directly ground to different sizes using hammer mill, pin mill, roller mill, or disc mill, and so on. Dry rice flour is used for baking, baby foods, extrusion-cooked products, and high-protein flour.

An alternative method, the freeze grinding process, has recently been proposed for producing rice flour with the advantages of zero water use, reduced energy consumption compared with the wet grinding process, and being environmentally friendly (Ngamnikom and Songsermpong 2011). This process involves initially soaking or freezing the rice kernels in liquid nitrogen prior to dry grinding in a dry grinding machine (hammer mill, roller mill, or pin mill). When comparing the efficiency of wet, dry, and freeze grinding processes, it was observed that wet grinding yielded a smaller average particle size and a lower percentage of

damaged starch than the alternative methods of grinding. Freeze grinding, particularly using the hammer mill for grinding, reduced both the average particle size and the damaged starch content due to the extremely low temperature of the kernel prior to grinding and gave a higher yield than dry grinding with an identical grinder. In addition, the energy consumption of freeze grinding was similar to dry grinding and much lower than wet grinding (Ngamnikom and Songsermpong 2011). Therefore, the freeze grinding process provides an economically effective alternative to the traditional wet grinding process.

Composition of rice grain and its milling fractions

The composition of the rice grain is greatly dependent on cultivar, and environmental and processing variability. Rice, like all cereals, is rich in complex carbohydrates, a source of proteins, minerals and vitamins mainly of the B-complex, and contains biofunctional components (dietary fiber and gamma-oryzanol). Salinity is one of the major threats to production of rice and other agricultural crops worldwide, which can reduce yield but also affects the kernel composition by increasing protein content due to glutelin enhancement, with simultaneous variations in the relative proportions of the individual peptides within the glutelin, and possibly involving other rice components such as starch and lipids (Baxter and others 2011).

In addition to the variations due to crop year that affect moisture, protein, ash, and fat contents, there are significant differences in the chemical constituents depending on the variety of rice grown. This variation is particularly significant for biofunctional components. Lu and others (2011) studied the chemical composition of six varieties (five japonica and one indica) of brown rice from Taiwan, showing that dietary fiber content ranged between 5.1 and 10.0%, and in all varieties the amount of insoluble dietary fiber was greater than that of soluble dietary fiber. The content of gamma-oryzanol varied from 17.9 to 29.2 mg /100 g and could reach up to 41.3 mg /100 g in some crops and was higher in the japonica types than in the indica type rice.

The milling process greatly affects the chemical composition of the rice kernel (Figure 5.2) due to the removal of the outer bran layers and their proteins, fats, and a large percentage of fibre, vitamins, and minerals. The characteristics of rice flours are governed by the inherent variations of the cultivars, environmental variation, the grinding methods, and their previous treatments. Usually rice flours have the same chemical composition as the parent-milled kernels.
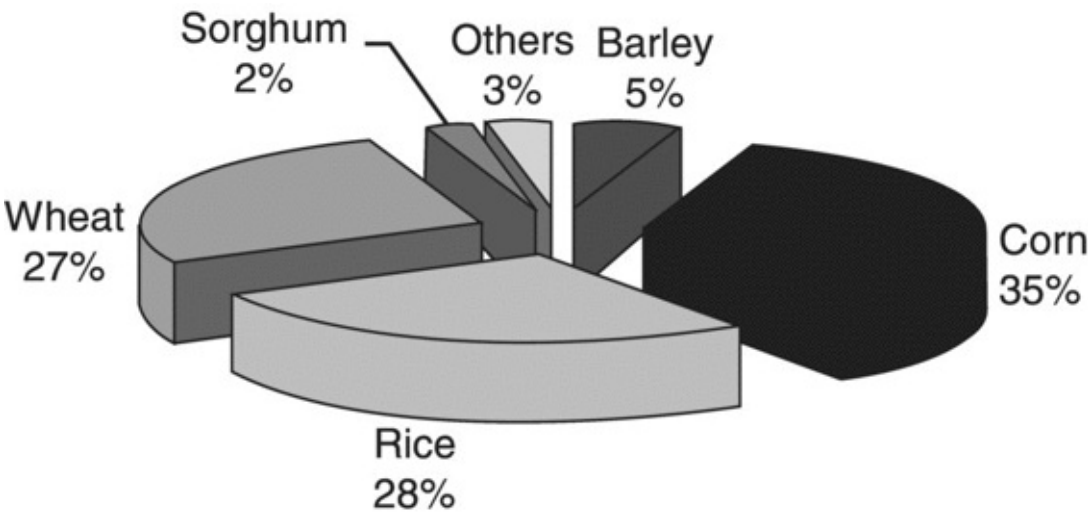
Figure 5.2 World's cereal production expressed as percentage. Data: FAOSTAT data corresponding to 2010.

Carbohydrates are the most abundant component in rice with a starch content of approximately 80% (14% moisture). Rice starch, as in other cereals, is a glucose polymer composed of amylose and amylopectin in different proportions depending on the rice variety.

The starch content of the rice grain increases from the surface to the core; thus, milled rice has s high starch content. Rice starch is considered non-allergenic because of the hypoallergenicity of the proteins associated with it. Protein is the second most abundant constituent of milled rice, ranging from 6.3 to 7.1 (g of N × 5.95). Protein concentration decreases from the surface to the centre of the kernel. In rice, the ratio of albumin–globulin–prolamin–glutenin is unique among the cereals, having a predominant concentration of glutelins, and reduced prolamins (Hamaker 1994). Similarly to other cereals, rice proteins are deficient in the essential amino acid lysine, but as a consequence of the protein fractions ratio, rice has a higher lysine content than other cereals. Note that although the amino acid pattern of the proteins could be similar in different rice varieties, significant differences have been encountered in the protein and starch digestibility among varieties (Acquistucci and others 2009). Lipids are not as abundant as starch and proteins, but they make an important contribution to the nutritional, sensory, and functional characteristics. Other components are fiber and minerals, although their amounts are greatly affected by milling. Iron, phosphorous, potassium, and magnesium are the most important minerals in rice. Like the other cereals, rice is a source of B-vitamins. An increasing awareness of functional foods has prompted the use of germinated brown rice for obtaining rice flour, which contains high levels of gamma amino butyric acid (GABA), but also induces an increase in reducing sugar and ash content, and a reduction in amylose (Xu and others 2012).

Rice is considered to be an important nutrional source of energy, providing 26% of the total energy intake in developing countries but only 4% of the total energy intake in the developed countries (Rosell 2004). In developing countries, rice supplies 20% of the dietary protein intake but because of its incomplete amino acid profile and the limited amount of micronutrients in milled rice, malnutrition is a widespread problem where rice is the staple food. Nowadays, different techniques for rice fortification have been developed to add essential vitamins and minerals to the grain (Rosell 2004; Wright Hoffpauer 2004). Ho and others (2006) reported the feasibility of fortifying rice flour with folic acid as a strategy to prevent the incidence of neural tube defects in Malaysia, where rice constitutes a staple food, since 85% of the women of reproductive age took at least one whole portion of cereal flour.

Rice flours types and their functional properties

There are more than 40 000 rice varieties worldwide that can be classified according to their original cultivation area, grain size, and amylose content. Indica rice has been grown in India, Bangladesh, Vietnam, Thailand, Pakistan, and so on, while Japonica rice is cultivated in Japan, Korea, and northern and central regions of China. Based on the grain size, rice can be classified as long (longer than 6.6 mm), medium (between 5.5 and 6.6 mm) and short (shorter than 5.5 mm). Rice is mainly consumed as polished rice and thus, primary differences among different types of rice rely on their cooking characteristics, although they also differ in their physicochemical properties (Vasudeva and others 2000). Starch determines the physical properties and functionality of the rice grains, and these properties are greatly dependent on the amylose/amylopectin ratio. Amylopectin is a branched polymer and is more abundant than the linear amylose polymer. However, amylose has received more attention from the scientific community because it is considered an indicator of cooking quality. Rice starch that lack amylose or contains less than 1% amylose is called waxy – because of its mutation at the waxy locus – or glutinous due to its opaque appearance. Complete information about rice starch structure and functional properties has been reviewed by Fitzgerald (2004).

The amylose content defines the gelatinization temperature of the starch and in general the pasting behavior and viscoelastic properties (Fan and Marks 1998; Singh and others 2000; Meadows 2002; Saif and others 2003; Yu and others 2012). Amylose content shows good correlation with important functional properties such as degree of starch crystallinity, the blue and turbidity values, swelling power, hardness, adhesiveness and stickiness, and also solubility (Iwashita and others 2011; Yu and others 2012). In addition, the amylose content also affects starch digestibility; specifically, at a higher amylose content there is high content of resistant starch (RS) and a reduced amount of slowly digested starch (SDS) (Zhu and others 2011). Nevertheless, Lin and others (2011) when they analyzed the behavior of 79 different rice genotypes, concluded that the amylose content, the protein content, the gel texture, and the gelatinization behavior could explain up to 80% of the variability observed in the flour properties. High protein content limits the pasting process due to the water uptake of the proteins which hinders starch swelling, this being necessary to increase the percentage of water and ensure proper cooking (Sun and others 2008). Similar findings were made by Baxter and others (2004) when the amount of prolamins were modified in rice flours.

Since pasting properties influence baking behavior, the rice cultivar used for grinding should be selected carefully when the flour is destined for the bakery. Generally, the varieties of long grains have a higher amylose content and gelatinization temperature and major tendency to retrograde than the varieties of medium or short grains. Rice flour from waxy rice varieties is not appropriate for baking, probably due to its low gelatinization temperature (61–62 °C), and the differences in the amylopectin chains, the enzymatic activity, and the protein content compared to non-waxy varieties (Zhu and others 2010). Flours from germinated rice, besides the changes in proximate composition, show different functional properties, namely, reduced solubility, paste viscosity, and percentage of retrogradation, as well as increased turbidity and swelling power (Xu and others 2012). The germination process shortens the length of the amylopectin and amylose chains due to enzymatic hydrolysis, which could be partly responsible for changes in the functional properties.

The environmental conditions also affect rice flour properties. For instance, rice kernels cultivated in salty conditions led to flours with higher pasting temperatures and lower peak and breakdown viscosities (Baxter and others 2011). Soil moisture stress during grain maturation also has an important impact on functional properties by reducing the protein content and increasing the swelling power, peak viscosity, gel hardness, and cohesiveness (Gunaratne and others 2011a). Appropriate soil fertilization increases crop yields, but also results in flours with a higher protein content and low apparent amylose level, as well asaltered properties during heating, such as enhanced pasting temperature, cold paste viscosity and setback, with low peak viscosity and breakdown (Gunaratne and others 2011b). Nevertheless, Dang and Copeland (2004) stated that the pasting properties are not solely determined by chemical composition (starch content, amylose, proteins, and lipids), but that minor constituents or enzymatic activities must have a role in the flour behavior.

The physical properties of rice flour are also affected by the time from grain harvest to milling and by the temperature used in the drying process prior to storage. Fan and Marks (1999) studied the effect of the duration and temperature of storage on rice flour properties using a differential scanning calorimeter, and noted a significant effect of storage time and temperature on the enthalpies and temperature of gelatinization and retrogradation of rice flour. Zhou and others (2003) also observed that the RVA pasting curves of rice flours from different cultivars changed with the time and temperature of rice storage. Breakdown decreased over time and the results indicated that rice storage led to protein changes such as an increase in the amount of high molecular weight peptides. In fact, the changes in the structure and properties of oryzenin, rather than starch, are responsible for the modification of the rice physical properties associated to storage (Teo and others 2000; Patindol and others 2003). Gamma irradiation has sometimes been used for reducing microbial growth during storage, but this technique caused the breakage of the amylopectin chains at the amorphous regions, hardly affecting the crystalline regions of starch granules, and reduced the pasting and gel viscosities of the flours, improving starch digestibility (Bao and others 2005; Zuleta and others 2006).

The grinding method also affects the functional properties of rice flour. Nishita and Bean (1982) reported a comparative study about the properties of rice flours obtained with different mills. Roller mills led to rice flours with medium particle size that showed a good baking performance. Conversely, burr mills yielded excessive coarse flour that produced low-quality breads. In contrast, rice flour ground in hammer mills had finer particles with high levels of damaged starch that were not adequate for bread making although they could be be used in cake production. Regarding the pasting properties, the flours with greater particle size present lower peak viscosity and final viscosity at 50 °C (low tendency to retrograde), while flours with medium and small particle size did not show any significant changes in their properties. Kadan and others (2008) also confirmed that rice flours ground in a pin mill had an even particle size, less tiny particles, and better performance for bread making than the flours obtained with Udy mills. The particle size of rice flours is usually lower than 200 μm, but it is possible to get ultrafine particles with hammer mill or dry jet grinding, with the consequent increase in the amount of damaged starch and altered pasting properties (Hossen and others 2011). Similarly, Tran and others (2011) confirmed that cryogenic milling reduced starch granule degradation compared to hammer milling, due to the increased grain brittleness and fracturability at cryogenic temperatures, reducing the mechanical energy required to diminish the grain size.

The enzymatic treatment of rice prior to grinding is a scarcely explored alternative for modifying flour properties. In this treatment, the kernel is moistened to ensure that the enzymes act on the rice constituents; thus, drying must be subsequently performed. Another necessary step is inactivation of the enzymes – usually by thermal treatment – to stop their action during further processing. Following this strategy, Satmalee and Matsuki (2011) increased the amount of resistant starch in rice flours by using pullulanase debranching followed by heat-moisture treatment. These treatments must be optimized for each type of ground rice as they also modify the pasting properties of the flours.

Rice flours are usually obtained from polished or milled kernels, although sometimes brown rice is used for grinding. Flours obtained from brown kernels have a temperature of gelatinization that is 13–17 °C higher and a gelatinization enthalpy that is about 40% greater than their milled counterparts (Normand and Marshall 1989). Nevertheless, brown rice flours have a very short shelf-life due to the presence of active lipase and lipooxygenase that releases free fatty acids, which become rancid imparting a bitter taste to the products. Reducing the temperature and humidity during storage, or even using inert atmospheres, extends the stability of these flours, but all these systems produce an additional cost that can rarely be justified. An alternative way of obtaining brown rice flour is by mixing milled bran to the already ground rice at appropriate levels. In this case, the bran can undergo prior chemical or physical treatments for ensuring its stabilization and extending its shelf-life (Champagne and others 1991; Champagne and Grimm 1995). A different approach is to remove the fat from the bran before it is added to the rice flour.

Processes such as parboiling the kernel before milling modifiy the physicochemical characteristics of rice. In the parboiling process, paddy rice is steamed under pressure to gelatinize the starch within the kernel; this process favors the migration of nutrients from the bran layer to the starchy endosperm. Parboiled rice has thus high amount of nutrients (vitamins and minerals) and different sensory properties. Flours obtained from parboiled rice produce soft and sticky doughs that it are susceptible to amylase action. Therefore, those flours are not adequate for bread making, but they can be used in small concentrations for cake production where the short process time reduces the activity of the amylases.

Pregelatinized rice flour is usually produced by extrusion, but it is also possible to obtain it by steam-jet cooking (Kim and others 2009), heating-stirring (Wu and others 2010), autoclave, and oven treatments (Takahashi and others 2005). The properties of this type of flour, especially flour obtained by extrusion, depend on the rice properties and the treatment conditions (moisture, temperature, time, and so on) (Kadan and others 2003; Hagenimana and others 2006; Guha and Ali 2011). All these processes modify the rheological properties of the flour increasing the cold viscosity and reducing the peak viscosity and the tendency to retrograde as the amount of gelatinized starch increases. In fact, Figure 5.3 shows the viscosity pattern of rice flours subjected to different intensity extrusion processes, depending on the temperature and moisture content. The extruded flours had low viscosity after cooking or heating. The extruded flours showed high cold viscosity and the viscosity degree was dependent on the treatment intensity. These changes reduce the viability of the flours for the bread making process, because they lead to sticky doughs and low volume breads, but small amounts can be added to increase dough consistency. Those flours are suitable for making sauces or batters, because they have low fat absorption ability.
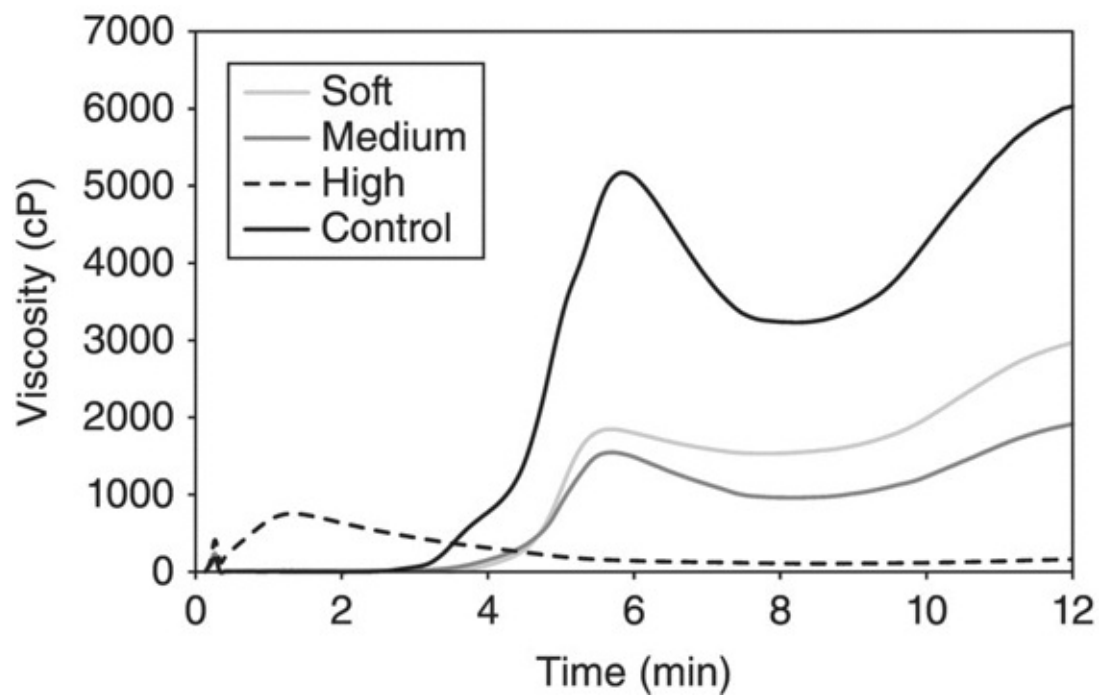
Figure 5.3 Pasting behaviour of extruded rice flours measured by a Rapid Viscoamylograph. Control: non-extruded rice flour; soft: rice flour extruded at low temperature; medium: rice flour extruded at intermediate temperature; high: rice flour extruded at high temperature.

Rice flour-based bread

Wheat is the cereal predominantly used in baking. Nevertheless, wheat free foods are becoming increasingly attractive for those people concerned about their health or wanting to avoid wheat in their diet. Gluten-free breads were products initially designed for people who have an intolerance to some specific peptides found in the gluten proteins, and the unique treatment is to keep their diet as gluten-free as possible. Particularly, gluten from wheat, rye, barley, triticale, and some varieties of oats must be eliminated from the diet of individuals with celiac disease. The unique cereals considered gluten-free safe are rice and corn, although rice flour is the most suitable commodity for bakery applications due to its bland taste, white color, digestibility, and hypoallergenic properties. Other attributes such as the low content of protein and sodium and the presence of easily digested carbohydrates are additional benefits. However, although rice flour has numerous advantages, rice proteins have relatively poor functional properties for food processing compared with other plant proteins. Rice proteins are extremely insoluble due to their hydrophobic nature (Lumdubwong and Seib 2000) and unable to form the viscoelastic dough necessary to hold the carbon dioxide that is produced during proofing of yeast-leavened bread-like products. The low content of prolamins in rice flours prevents the formation of a protein network when rice flour is kneaded with water. As a consequence, the carbon dioxide produced during fermentation cannot be retained, yielding a product with a low specific volume that does not resemble the soft and open structure of wheat bread. Nevertheless, the type of rice milling and the resulting particle size of the flour define the suitability of the rice flour for bread making (Song and Shin 2007). Considering that initial pasting and setback viscosities decrease with decreasing particle sizes, wet-milled rice flours that have higher apparent viscosity and smaller particle sizes than dry-milled rice flour show better properties for making gluten-free rice bread (Song and Shin 2007). In addition, rice cultivars with intermediate amylose content, which are also sticky and soft, yield cooked rice bread with a high volume (Iwashita and others 2011). A chemical modification of the rice flour has been also proposed for improving its baking functionality (Nabeshima and El-Dash 2004). A recent proposal for improving rice flour potential for bread making is the addition of glutathione to rice that improves its gas-retaining properties (Yano 2010). Glutathione prevents the formation of the disulfide-linked macromolecular protein barrier, which facilitates the deformation of rice batter, thus increasing its elasticity in the early stages of bread baking and the volume of the resulting bread (Yano 2010).

The inability of rice flour to hold carbon dioxide in fermented products can be overcome by using different structuring agents. Among the cellulose derivatives, hydroxypropyl methylcellulose (HPMC) seems to be the best gluten substitute for rice bread formula due to its gas retention capacity and its properties as a crumb structuring agent (Gujral and others 2003a). With the addition of HPMC it is possible to obtain rice flour dough with a similar consistency and rheological properties to those of wheat dough (Sivaramakrishnan and others 2004). Other gums such as locust bean gum, guar gum, carrageenan, xanthan gum, and agar have been tested as gluten substitutes in rice flour bread but the addition of HPMC or the combination of HPMC and carboxymethylcellulose (CMC) resulted in the highest specific loaf volume due to their ability to trap fermented gases ([Figure 5.4](#)) (Cato and others 2004). In contrast to xanthan gum or guar gum, HPMC does not modify the pasting properties of rice starch during heating and only changes the viscosity during cooling (Rosell

and others 2011). A rheological study carried out on rice starch revealed that the incorporation of hydrocolloids in the rice starch pastes produced weaker structures with less gel-like character than starch, which might be because the intermediate network structure had a reduced number of junctions zones with the starch combined with hydrocolloids entanglements (Rosell and others 2011).
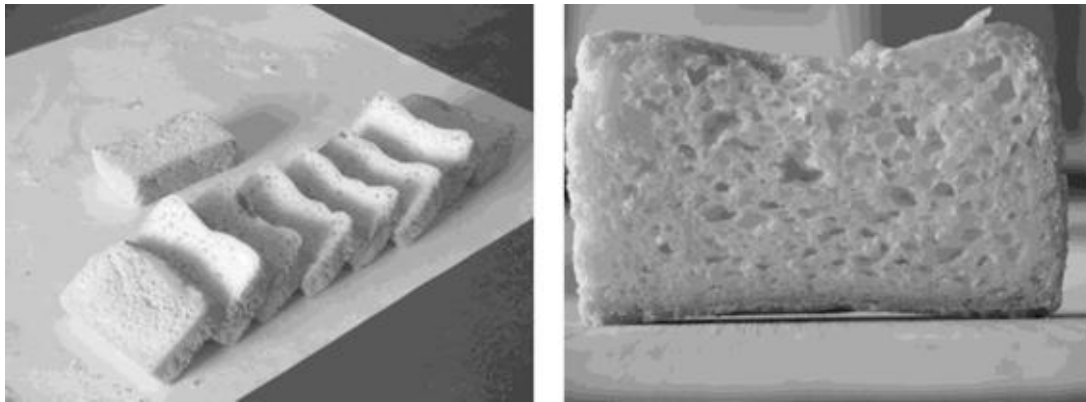
Figure 5.4 Rice-based bread with 4% HPMC. (Photo by Cristina M. Rosell)

Further improvement of the crumb texture has been obtained with the addition of different enzymes. The addition of cyclodextrin glycosyl transferase to the rice bread formulation led to rice loaves with very soft crumbs and extended the shelf-life (Gujral and others 2003a, 2003b). Other useful enzymes in rice bread formulation are glucose oxidase and transglutaminase (Gujral and others 2004a, 2004b). These enzymes allowed a decrease in the quantity of structuring agents needed to obtain rice bread with an acceptable quality by catalyzing the formation of intermolecular and intramolecular cross-links between the rice proteins, resulting in a protein network. However, to overcome the possible limitation derived from the reduced amount of rice proteins, it the incorporation of different proteins isolates (pea, soybean, egg albumen, and whey proteins) has been proposed for creating a network-like structure in rice-based doughs and at the same time enriching the products (Marco and Rosell 2008a, 2008b). Protein cross-linking among proteins catalyzed by transglutaminase was confirmed by a decrease in the amount of free amino groups and the disappearance of numerous protein bands as a consequence of the formation of large protein polymers, linked by isopeptidic and disulfide bonds, with reduced solubility (Marco and others 2007, 2008). Soy protein is frequently added to gluten-free bread formulations because it improves the bread texture (Sodchit and others 2003). The combination of rice flour with 13% soybean protein isolate, 4% HPMC, and 1% transglutaminase produced gluten-free breads, where the decrease in the specific volume induced by soybean proteins was partially counteracted by the HPMC, also decreasing the crumb hardness, while transglutaminase gave a more continuous structure of the crumb (Marco and Rosell 2008c). The addition of soybean or pea proteins to rice flour improve the amino acid balance since legume and cereal proteins are complemented in the essential amino acids lysine and methionine improving the protein biological value of the rice products.

A very common approach for obtaining gluten-free bread from rice flour is the use of flours or starch blends. Complex formulations – including corn starch, brown rice, soy, and buckwheat flour – for obtaining gluten-free bread in the presence of dairy products like skimmed milk powder have yielded a network-like structure resembling the gluten network in wheat bread crumb (Moore and others 2004). A combination of rice flour (45%) with corn (35%) and cassava (20%) starches gave also a good gluten-free bread with uniform cells well-

distributed throughout the crumb and a pleasant flavor and appearance (Lopez and others 2004). Rice flour mixed with 46.5% chestnut flour, xanthan gum, and different emulsifier contents was used to prepare breads which were baked using 40% infrared and 30% microwave power for 9 min that had comparable quality with conventionally baked ones (Demirkesen and others 2011). Blends of buckwheat and rice flour in the presence of hydrogenated vegetable fat also gave gluten-free breads with good sensory acceptance (Torbica and others 2010). Husked and unhusked buckwheat flours affect rice flour rheology to different extents (Torbica and others 2010). Gluten-free products containing unhusked buckwheat flour (up to 30%) had higher water absorption values, lower stability, and a weaker protein network structure, as well as a lower peak viscosity than those with husked buckwheat flour, and both types of buckwheat flours increased the crumb hardness (Torbica and others 2010).

Currently, different flour blends with added nutritional value are being proposed because the nutritional value of foodstuff is the market target. This concern is even greater in gluten-free diets, which are characterized by an unbalanced intake of different nutrients. A recent report indicates that gluten-free breads make a very small contribution to the recommended daily intake of protein, a large contribution to the carbohydrate dietary reference intake, while their fat and dietary fiber content shows great variation (Matos and Rosell 2011). These results indicate the importance of designing nutritionally balanced or enriched gluten-free products. Rice flour blended with up to 30% buckwheat flour led to gluten-free breads with an enhanced content of total phenolic compounds, rutin and quercetin contents, and antioxidant activity (Sakac and others 2011). The incorporation of deffated rice bran in bakery products has been proposed for improving the nutrient profile. It has been reported that the dietary fiber content and total antioxidant activity of bread increase with increasing levels of deffated rice bran, with an addition of up to 15% being acceptable as well as improving shelf-life (Sairam and others 2011). Even rice bran oil that has a higher content of the essential fatty acid linoleic acid (34.98%) compared to that of common bakery shortening (5.14%) has bakery applications in which it replaces bakery shortening (Kaur and others 2012).

Pregerminated brown rice is another alternative bread ingredient because it is more nutritious after germination. The substitution of pregerminated brown rice flour for wheat flour improves bread quality. Overall liking scores of these breads revealed that germinated brown rice flour could be incorporated up to 50% by weight in bread formulations without compromising sensory acceptability (Charoenthaikij and others 2010, 2012). In addition, germination (steeping at pH 3 for 24 h at 35 °C) increased free gamma aminobutyric acid from 2.11 to 32.7 mg per 100 g flour for wheat/germinated brown rice (Charoenthaikij and others 2012).

Rice flour in cake making

The term cake includes various different baked products which differ in their formulation and preparation. A common factor in all these products is the formation of batter to incorporate air in the dough and a further baking. During baking, the batter expands either due to the volume increase of the internal gases or the action of a leavening agent (baking powder or yeast). Cakes can be classified into two groups: the layer and pound cakes and the angel and sponge cakes. The first group includes homemade cakes and the muffins ([Figure 5.5](#)), which are fat based with a structure is the result of fat-in-water emulsion formation during battering. The second group is made up of sponge cakes, usually containing cream or fruit fillings. They are less dense due to the major incorporation of air.

Figure 5.5 Gluten-free muffins. (Photo by Manuel Gómez)

In cake production, a gluten network is not developed, thus it is possible to make cakes with starchy raw ingredients. The percentage of protein affects the quality of the cakes, however, so a common practice is to blend starches and proteins from different sources (Ronda and others 2011) or to add ingredients with a high protein content such as eggs. Rice flour can be used as the main ingredient to produce cakes with similar qualities to wheat cakes (Sae-Eaw and others 2007). Alternativiely, rice flour can be blended with wheat flour, and this practice is sometimes used to reduce costs.

One of the main difficulties when using rice flour in baking is its lack of uniformity because it is obtained from broken kernels without any previous classification of their functional properties; and those greatly affect the cake quality as illustrated Bean and others (1983). These authors found that rice varieties with medium or short grains, low amylose content, and low gelatinization temperatures gave cakes with superior textures compared with those made from long grain rice, which had excessive dry and sandy textures. Similarly, Ha and others (2007) found quality differences among cakes produced with rice flour from different varieties, and they noted that the importance of rice hardness as well as pasting properties . Actually, the softest varieties yielded finer flours and resulted in cakes of better quality. A linear relationship has also been found between the volume of steamed leavened rice cakes and the amount of amylopectin, with 1 : 8 being the optimum amylose : amylopectin ratio

(Mohamed and Hamid 1998). Rice flour with a high content of amylopectin gave cakes with a texture that was too elastic and sticky.

It is possible to make cakes with different types of rice flours, although the formulation should be modified according to the amylose content and the gelatinization temperature. Cakes made from rice flour with a high amylose content require an increase of the amount of water in the recipe. Volume and appearance of cakes prepared with rice flour with a high gelatinization temperature can be improved by either reducing the amount of sugar in the recipe (sugar increases the gelatinization temperature of the starch) – although cakes with a coarser texture are obtained (Perez and Juliano 1988) – or adding different proteins. Mohamed and others (1995) and Mohamed and Hamid (1998) studied the effect of adding several proteins to the formulation of steamed leavened rice cakes made from rice flour, sugar, water, and yeast or baking powder. They found that the addition of skimmed milk powder and egg yolk improved the volume and texture of the cakes, while adding soy protein, gluten, and whey powder reduced their quality.

Sometimes blends of different flours or starches are used in the production of cakes. For instance, butter cakes made with a blend of rice flour, cross-linked rice flour, and pregelatinized tapioca starch powder had a similar quality to wheat cakes (Varavinit and Shobsngob 2000). The pregelatinized tapioca starch acted as a binder giving firmness to the cake structure. Cakes have been also prepared mixing rice flour with some starches (maize and cassava) (Schamne and others 2010), or blending rice flour with legume or pseudocereal flours such as buckwheat (Levent and Bilgicli 2011; Gularte and others 2012a). The legume flours have major content of proteins than the rice flour, because of that lentil, bean, chickpea, and pea flours have been used for enriching rice cakes (Gularte and others 2012a). Usually that practice is aiming at reducing costs, improving the nutritional value of the products or obtaining different tastes and flavors. Recently, some fibers (inulin, guar gum, oat fiber) have been incorporated in rice cakes and the combination of oat fiber–inulin resulted in better gluten-free cakes from the instrumental and nutritional point of view (Gularte and others 2012b).

In general, flour from glutinous rice is not used in the production of cakes or similar products in Western countries. Conversely, Eastern countries have some traditional cakes obtained from glutinous rice, such as MiGao ormochi. The MiGaois a steam-cooked Chinese cake prepared with blends of glutinous and non-glutinous rice, and its quality can be improved with the addition of hydrocolloids (Ji and others 2010a). In this type of cake, starch retrogradation affects the cake texture, and the increase in hardness during storage has been associated to amylopectin retrogradation (Ji and others 2007, 2010b). Themochi is an Asian specialty made with glutinous rice and sugar among other ingredients (Chuang and Yeh 2006a); this cake can be also prepared by extrusion (Chuang andYeh 2006b). Flour from glutinous rice is sometimes added to improve the quality of rice cakes so they have similar characteristics to wheat cakes (Chueamchaitrakun and others 2011). Rice flour has different pasting properties to wheat flour as well as a greater tendency to retrograde, giving a harder crumb texture which can be softened by adding glutinous rice flour. In some cake formulations, waxy rice flour is used as an ingredient, for instance to replace up to 5−25% of the wheat flour in a muffins recipe to increase moisture retention during baking (Johnson 1990).

Recent researches has focused on improving the quality of rice cakes by incorporating

hydrocolloids. Xanthan gum added in small amounts improves the volume and texture of cakes as well as the sensorial characteristics, and it also delays crumb hardening (Preichardt and others 2011). Xanthan gum individually or added in combination with guar gum has been an effective improver in cakes made in conventional ovens or microwaves (Sumnu and others 2010; Turabi and others 2010a). In addition to their water retention ability, xanthan gum and guar gum increase the dielectric constant and loss factor values of batters, improving cake performance when baking with microwaves (Turabi and others 2010b). The addition of emulsifiers in combination with xanthan gum also improves the quality of rice cakes (Turabi and others 2008a, 2008b; Ronda and others 2009). Emulsifiers favor the incorporation of air in the batters, leading to small and uniform air bubbles that are stable during baking resulting in cakes with a high volume and crumbs with small, uniformly distributed air cells.

It has been also proposed to use enzymes for improving cake quality, although this practice is not common at the industrial level because processes are very short. However, extending the cake making process to favor the action of starch degrading enzymes would make it possible to minimize the retrogradation phenomena and to extend the cake's shelf-life. In fact, a thermostable 4-alpha-glucanotransferase from *Thermus scotoductus* that hydrolyzes the amylose and reduces the length of the amylopectin chains has been effective for reducing the hardness of rice cakes during storage (Seo and others 2007).

Another ingredient from rice milling that has been used in cake making is rice bran. However, contradictory results have been reported when rice bran was incorporated in wheat cakes. Lebesi and Tzia (2011a) concluded that the inclusion of rice bran reduces the specific volume of cakes and their sensory acceptance and increases crumb firmness; in addition, the shelf-life of the cakes was extended with endoxylanases (Lebesi and Tzia 2011b).

Use of rice flour in cookies production

There is a world spread production of rice cookies due to both cultural reasons, like in some areas of Asia and America, and looking for gluten-free products. The rice flour requirements for cookie production are greatly dependent on the type of cookies. In processes where a gluten network is not developed it is possible to completely replace the wheat flour with starchy materials, such as in the short dough for wafers. Conversely, in the production of hard dough, where the development of a gluten network is required, rice flour will solely able to partially replace the wheat flour reducing dough elasticity in the process.

There is scarce scientific literature concerning rice cookies. An optimized formulation for cookies was obtained with brown rice flour (70%), soy flour (10%), corn starch (10%) and potato starch (10%) (Schober and others 2003). The resulting product was comparable to wheat cookies, although with better overall acceptability.

Blends of wheat and rice flour have been used in the production of cookies. Gujral and others (2003c) described that the substitution of up to 20% rice flour for wheat flour produced a less cohesive and more adhesive dough. Rice flour performance in cookies making depends on the type of flour. Ha and others (2007) reported that flours from varieties with greater protein content and low cohesiveness and adhesiveness behave better in cookies processing.

Rice bran has been also added to wheat cookies to increase the fiber and protein content, as well as the level of lysine (Sharma and Chauhan 2002). Cookies containing 10% rice bran showed higher spread factor than those without bran, but the effect was significantly dependent on the bran treatment, being higher in the bran stabilized by dry heat than in extrusion cooking stabilized bran. In general, the sensory perception of products – particularly the taste and texture – decreases when increasing the amount of bran rice but it is possible to obtain acceptable products containing up to 10% rice bran (Saeed and others 2009). Alternatively, the use of protein concentrates extracted from rice bran has been proposed for increasing the protein content of cookies (Yadav and others 2011). In some cases, extracts from rice bran have been added to reduce fat oxidation in cookies (Bhanger and others 2008), and the same effect can be obtained with defatted rice bran (Watanabe and others 2010).

Other bakery rice-based products

Some bread specialties have been adapted to obtain gluten-free products for people with gluten intolerance. This is true for chapati, unleavened bread made from whole wheat in India. The use of different hydrocolloids (HPMC, guar gum, xanthan gum, locust bean gum) and α-amylase in the formulation of rice flour chapati improved the texture by keeping its extensibility during storage (Gujral and others 2004c). In addition, hydrocolloids and α-amylase delayed amylopectin retrogradation, keeping the chapatis fresher for longer. In other cases deffated rice bran has been used for enriching wheat chapaties, namely up to 20% deffated rice bran has been added to wheat flour and chapatis were rated acceptable with the benefit of having a higher ash and total dietary fiber content than wheat chapati (Yadav and others 2012).

Rice flour has been used in the production of donuts. This product is obtained from a batter with a ring shape that is fried for 1–2.5 min, giving it a bright external color, crunchy crust (due to the dehydration of the outer part), and a spongy inner crumb due to the expansion produced by the leavening agent. A comparison of donut made with wheat flour, waxy rice flour, and long grain rice flour showed that donut made with waxy rice flour had less oil uptake, and that oil uptake could be reduced by adding pregelatinized rice flour (Shih and Daigle 2002). In addition, products made using rice flour had less dough consistency and were harder with less moisture content and higher oil absorption (Shih and others 2001). In contrast, the use of pregelatinized rice flour or acetylated rice starch yielded higher dough consistency, and a donut with a higher moisture content and less oil uptake.

Gluten-free pancakes have been prepared using rice flour or blends of rice flour and sweet potato flour (Shih and others 2006). The incorporation of sweet potato flour decreases the hardness and chewiness of pancake. The nutritional properties of rice–sweet potato pancakes were comparable with those of their wheat counterparts for protein content, dietary fiber, total carbohydrate, and calories.

Rice is one of the most consumed cereals, mainly as milled rice. However, a number of different value-added rice products have been developed prompted by the unique nutritive properties of this grain. As well as the use of rice as table rice, there is a high consumption in beer production, baby foods, breakfast cereals, confections, desserts, and also in bakery. The increased use of rice for food processing has been the result of an increasing consumer demands for healthier products, more convenient products and also a growing people interest in a variety of ethnic products. Among all the processed rice-based products that are being launched, bakery products have received special attention. The usefulness of rice flour for wheat bread substitution in the gluten-free diet of celiac patients has motivated the increase of bakery products.

Acknowledgments

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6

Barley, Maize, Sorghum, Millet, and Other Cereal Grains

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Introduction

According to the Food and Agriculture Organisation (FAO 2006), per capita cereal consumption fell from 171 kg per person per year in 1989–1991 to 165 kg in 1999–2001and 147 kg in 2007, as well as for the developing countries overall (from 174 kg to 166 kg and 146 kg). FAO estimations anticipate that the share of cereals in total calories will continue to decline, but very slowly, falling for the developing countries from 54% at present to 49% in 2030 and to 46% in 2050. Per capita consumption of cereals for all uses (including food, feed, and other nonfood uses, for example for seed and the production of ethanol or starch) should keep growing again after the reversal of the sharp declines of the 1990s in the feed sector of the transition economies (Figure 6.1). Food consumption of *coarse grains (maize, barley, oat, sorghum and millet)* has declined on average, but continues to be important mainly in sub-Saharan Africa (where it accounts for 70% of food consumption of cereals, with some countries depending overwhelmingly on maize – for example, Zimbabwe, Zambia – and others mostly on millet and sorghum – mainly the countries in the Sudano-Sahelian zone and to a smaller extent in Latin America (42%, mostly maize) (Table 6.1).
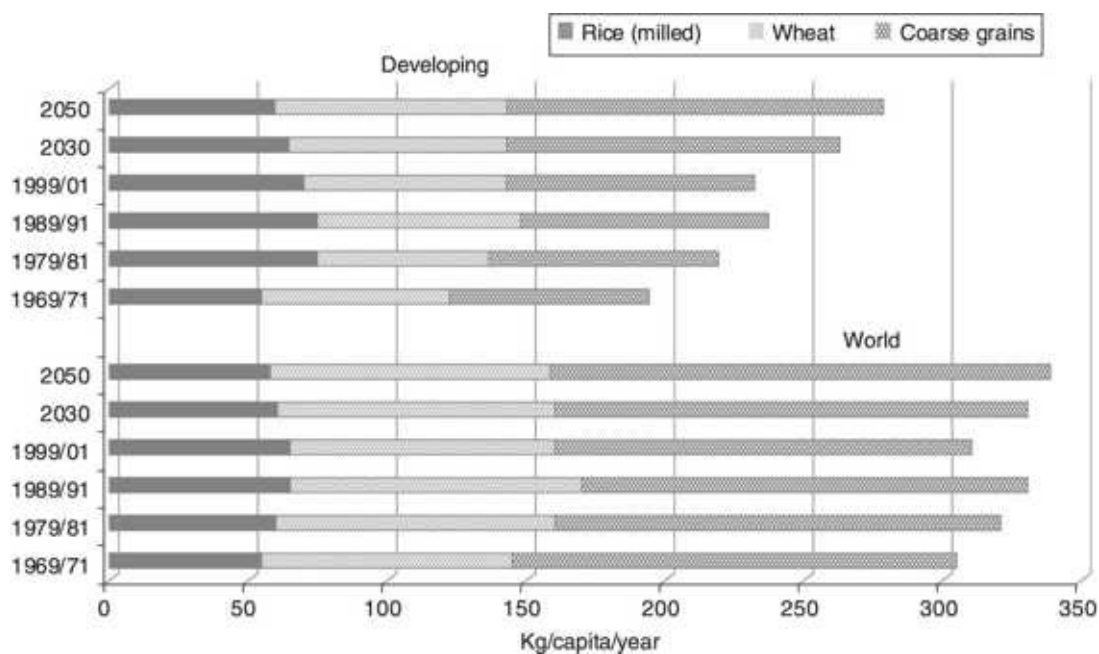
Figure 6.1 Per capita consumption (all uses) of individual cereals. (Adapted from FAO 2006).

Table 6.1 Cereal share of total energy, protein and fat supply

Source: http://faostat.fao.org/ accessed December 2011. (Adapted from FAO 2011).

Grain	Cereal supply, per capita	Energy supply, per capita		Protein supply, per capita		Fat supply, per capita	
	(g/day)	kcal/day	% of total energy	g/day	% of total protein	g/day	% of total fat
Total cereals							
World	402	1290	46	32	42	6	7

Africa	396	1225	50	33	52	8	16
America	331	967	30	25	27	5	4
Asia	428	1436	54	34	47	6	9
Europe	360	1001	29	30	29	4	3
Oceania	250	748	24	24	23	3	2
Maize							
World	46	139	5	3	4	1	1
Africa	112	358	15	9	15	3	7
America	94	286	9	7	7	2	2
Asia	24	69	3	2	2	1	1
Europe	19	53	2	1	1	0	0
Oceania	12	35	1	1	1	0	0
Barley							
World	3	7	0	0	0	0	0
Africa	9	25	1	1	1.1	0	0
America	1	4	0	0	0	0	0
Asia	1	3	0	0	0	0	0
Europe	4	8	0	0	0	0	0
Oceania	0	1	0	0	0	0	0
Oat							
World	1	3	0	0	0	0	0
Africa	0	1	0	0	0	0	0
America	5	9	0	0	0	0	0
Asia	0	0	0	0	0	0	0
Europe	5	12	0	0	0	0	0
Oceania	6	14	0	1	1	0	0
Sorghum							
World	11	33	1	1	1	0	0
Africa	50	151	6	5	7	1	3
America	2	5	0	0	0	0	0
Asia	6	18	1	1	1	0	0
Europe	0	0	0	0	0	0	0
Oceania	0	0	0	0	0	0	0
Millet							
World	11	32	1	1	1	0	0
Africa	37	107	4	3	4	1	2

America	0		0	0	0	0	0	0
Asia	9		27	1	1	1	0	0
Europe	1		3	0	0	0	0	0
Oceania	0		0	0	0	0	0	0

Developments in maize use for the production of sweeteners have boosted the food consumption of coarse grains in industrial countries, mainly in the United States. Overall demand for coarse grains will be increasingly influenced by the demand for animal feed and, in some countries, for the production of biofuels. The developing countries will be playing a growing role in the world total demand and trade of coarse grains. Wide inter-country differences in cereals food consumption will continue to persist. While the average of per capita food consumption of cereals is 147 kg/year (Table 6.1), several countries have per capita numbers under 100 kg/year, and some below 50 kg/year (Congo DR, Burundi, Rwanda). The countries with the highest food consumption of cereals are also in Africa, namely those in North Africa, but also Niger, Burkina Faso, and Lesotho, with per capita levels from 200 to 250 kg. Total utilization of coarse grains is forecast to increase marginally (< 1%) in 2011–2012, to 1156 million tonnes, below its 10-year trend, as growth in the demand for feed is forecast to slow down due to a higher intake of wheat and non-grain feed ingredients. The industrial use of coarse grains is also rising at a much slower pace than in the past, mainly because of stagnating maize-based ethanol production. Consumption of coarse grains should continue to grow, mainly for non-food uses (essentially animal feed, though use for the production of biofuels may assume some importance in the future) but also for food in many sub-Saharan Africa countries where coarse grains (maize, millet, sorghum, but also teff in Ethiopia) are the mainstay of cereals consumption. In developed countries, the concept of using South American, African, and Asian traditional raw materials and fermented foods as a template for wheat, wheat-free, and gluten-free based foods, particularly in Europe and North America, is in good accordance with the interest in westernized countries for ethnic foods with enhanced nutritional value. Strong immigration movements are making indigenous coarse-grain-based foods from different cultures and civilizations with ethnic eating habits available in a globalized world that embraces the use of traditional raw materials as ingredients in novel foods. The next three decades will probably see a higher increase in the global totals of coarse grains than the preceding three decades which witnessed the drastic contraction of feed use in the formerly centrally planned economies of Europe. Developing countries will increase their share of world non-food consumption of coarse grains and surpass the rest of the world by 2030. They now account for 39% of the world non-food use of coarse grains, up from only 17% three decades ago. The share may increase to 52% in 2030 and on to 56% in 2050 (Figure 6.2).
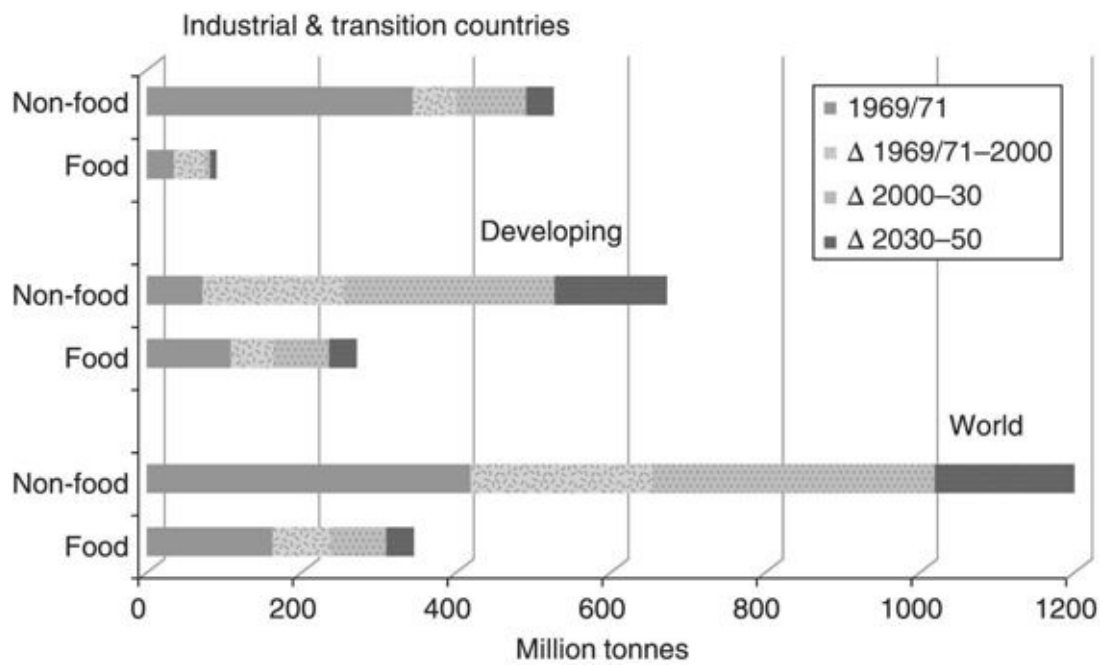
Figure 6.2 Coarse grains: food and non-food uses.

Source: (Adapted from FAO 2006).

Ethnic goods from coarse grains across the continents

Among the major coarse grains, maize represents either the major staple or main supplementary staple for 1000 million people in developing regions, mostly in sub-Saharan Africa. In Latin America, white and yellow maize is extensively used to make unleavened bread ('tortilla'), and also eaten 'on the cob', while in sub-Saharan Africa, white maize is processed into various products, but popular forms include starchy pastes such as porridge. In the Near East, maize flour is commonly used to make bread, while in South and South East Asia (notably Indonesia and the Philippines) it is consumed in a number of diverse ways. The different size fractions of grit that are produced during dry milling of maize vary in composition and end-use suitability (Singh and others 2011). Flaking grits are used for making "maize flakes." Coarse and medium grits are used in the processing of breakfast cereals and snack foods. Fine grits are preferred in porridge making and also used as a brewing adjunct, often to reduce the cost of beer. Coarse or granulated meal is used in pancakes, muffin mixes, and various bakery products. Finely ground maize is used in the production of "tortilla". Tortilla is an important product for the population of suburban and rural areas of Meso-American countries, such as Mexico and Guatemala. Tortillas are prepared from white, yellow, and blue maize; however, white maize is preferred in commercial processing. Similar bread made from maize in South America is called "Arepa," which has greater thickness compared to tortillas. Wheat meal is generally used for making unleavened bread called chapattis (roti) in India and Pakistan. However, maize meal is also used to prepare roti in winter and is very popular in north Indian states. Yellow maize meal is preferred in the preparation of roti. Roti made from maize meal is less pliable compared to that from wheat meal due to the differences in composition and rheological properties. Maize meal is kneaded into soft pliable dough with water for roti making. Maize meal dough lacks the viscoelasticity of wheat dough; therefore, warm water is used during kneading. Warm water helps in aggregation of the particles due to the partial gelatinization of starch. The physicochemical, functional, and chapati-making properties of flours from different maize varieties grown in India have been related to the properties of their starches (Sandhu and others 2007).

Millet and sorghum are major foods for around 60 million people concentrated in the inland areas of tropical Africa, who consume them mainly as fermented or unfermented preparations. These grains are also found in diets in large parts of India and Pakistan, where they are consumed predominantly as unleavened bread. Major sorghum food products throughout Africa are porridge, kisra, and injera. Porridge is prepared by cooking sorghum flour with water at different pH values. Different pH treatments affect the nutritional value of sorghum porridge. Lactic acid fermentation alleviates the adverse nutritional effects caused by boiling and alkaline pH (Taylor and Taylor 2002) regarding protein digestibility, starch digestibility, increased levels of B vitamins, reduced antinutrients such as tannins and phytic acid, and making the porridge product microbiologically safe (Taylor and Dewar 2000). In North Africa and India, sorghum flour is widely used to make flatbreads such as kisra (Sudan) and injera (Ethiopia and Eritrea) that involve lactic acid fermentation. The resulting flatbreads are moist and flexible and have a cellular structure formed by the fermentation gases (Taylor and Anyango 2012). In contrast, the major Indian sorghum flatbread, known as roti or chapati, is a thin, dry, crisp product with a puffed texture due to steam production

during baking. Fortification with cowpea affects the texture and taste of traditional African sorghum foods to an extent that largely depends on the sorghum cultivar concerned. Instrumental texture analysis relates well with the human perception of sorghum food texture and can rapidly predict the effects of fortification with legumes on such foods (Anyango and others 2011).

Oats have numerous uses in food; most commonly, they are rolled or crushed into oatmeal, or ground into fine oat flour. Oatmeal is chiefly eaten as porridge, but may also be used in a variety of baked goods, such as oatcakes, oatmeal cookies, oat muffins, and oat bread (Figure 6.3). Oats are also an ingredient in many cold cereals, particularly muesli and granola. Oats may also be consumed raw, and cookies with raw oats are becoming popular. Oats are also occasionally used in several different drinks. In Britain, they are used for brewing beer. Oatmeal stout is one variety brewed using a percentage of oats for the wort. A cold, sweet drink made of ground oats and milk is a popular refreshment throughout Latin America. Oatmeal caudle, made of ale and oatmeal with spices, was a traditional British drink. Historical attitudes towards oats have varied. Oat bread was first manufactured in Britain, where the first oat bread factory was established in 1899. In Scotland, they were, and still are, held in high esteem, as a mainstay of the national diet. In Scotland, a dish called sowans was made by soaking the husks from oats for a week, so that the fine, floury part of the meal remained as sediment to be strained off, boiled and eaten. Oats are also widely used there as a thickener in soups, as barley or rice might be used in other countries.

Figure 6.3 Commercial wholemeal oat cookies and home-made oat muffins. Photography and composition by Henar Gutiérrez Collar.

Among the other coarse grains, barley is popular in North Africa and the Near East, where it

is used to make bread and as an ingredient added to soup dishes. It is also widely eaten in parts of East Asia (Republic of Korea and Japan particularly), where it is added to rice. Rye is commonly used to make bread in many developed countries, particularly those in Northern and Eastern Europe, but also in areas of North Africa and the Near East (FAO 2006).

Coarse cereal commodities: production, consumption, share of calories and categories of use

Maize

Maize (*Zea mays*), also known as corn, is a major cereal grown throughout the world, and approximately 800 million tons of maize is produced worldwide, accounting for 35% of the total cereal production and 32% of the total area harvested for the year 2010 (Table 6.2). Maize provides 15% of total calories and protein, and 7% of fat in Africa (Table 6.1). More than 50% of total maize is produced in America (Table 6.2). Grain or whole meal, coarse, bolted and meal, fine, bolted and de-germinated maize account for 8.4–9.5% of protein, 1.2–4.3% of fat, and 73–78% of total carbohydrates (Table 6.3). The United States (41%), China (19.4%), European Union-27 (7%), Brazil (6.9%), and Argentina (2.8%), were the main maize-producing countries in 2009–2010 (US Grains Council 2012). Maize of different types (flour maize *Z. mays var. amylacea*, flint maize *Z. mays var. indurata*, dent maize *Z. mays var. indentata*, sweet maize *Z. mays var. saccharata* var. *rugosa*, popmaize *Z. mays var. everta*, waxy maize *Z. mays var. ceratina*, and amylo maize) and color (ranging from white to yellow, red, and purple) is grown (Singh and others 2011). Interest in pigmented maize rich in anthocyanins or carotenoids and phenolic compounds having antioxidant and bioactive properties has increased due to their health benefits. Although used primarily to feed livestock, maize is a versatile grain with a wealth of uses. It is also processed into a multitude of food and industrial products, including starches, sweeteners, maize oil, beverage and industrial alcohol, and fuel ethanol. Thousands of foods and other everyday items – from toothpaste and cosmetics to adhesives and shoe polish – contain maize components. Breakdown of maize utilization in the United States, the world's top maize producer and exporter, accounts for 39.4% (feed and residual), 45.4% (food, seed and industrial including ethanol), and 15.2% (exports) according to WASDE (2010).

Table 6.2 Total cereal and coarse grain production (million metric tons, MMT) and area harvested (million hectares, MHa) in 2010

Source: http://faostat.fao.org/ accessed December 2011. (Adapted from FAO 2011).

Grain	Production		Area harvested	
	MMT	%	MHa	%
Total cereals		100		100
World	2433	100	682	100
Africa	156	6	104	15
America	643	26	121	18
Asia	1193	49	328	48
Europe	406	17	110	16
Oceania	35	1	20	3
Maize		**34.7**		**23.7**
World	844	100	162	100

Africa	64	8	31	19
America	448	53	63	39
Asia	246	29	54	33
Europe	86	10	14	9
Oceania	1	<1	<1	0
Barley		**5.1**		**7.0**
World	124	100	48	100
Africa	6	5	5	10
America	16	13	5	10
Asia	20	16	11	23
Europe	73	59	23	48
Oceania	8	6	4	9
Oat		**0.8**		**1.3**
World	19.6	100	9.1	100
Africa	0.2	1	0.2	2
America	5.1	26	2.0	22
Asia	1.0	5	0.5	5
Europe	11.9	61	5.6	62
Oceania	1.4	7	0.9	9
Sorghum		**2.3**		**5.9**
World	55.6	100	40.5	100
Africa	20.9	38	24.8	61
America	22.5	41	5.9	15
Asia	9.9	18	9.1	23
Europe	0.7	1	0.2	0
Oceania	1.6	3	0.5	1
Millet		**1.2**		**5.2**
World	29.2	100	35.1	100
Africa	15.2	52	21.1	60
America	0.3	1	0.2	0
Asia	13.3	46	13.5	39
Europe	0.3	1	0.3	1
Oceania	0.0	0	0.0	0

Table 6.3 Coarse grain composition and energy content

Source: http://www.fao.org/docrep/X5557E/X5557E00.htm. (Adapted from FAO 1953).

Cereals	Carbohydrate						
	Water	Protein	Fat	Total	Fiber	Ash	Energy
	g/100 g of edible portion						kcal/ 100 g
Maize (corn)	0	0	0	0	0	0	0
Grain or whole meal	12	9.5	4.3	72.9	2.1	1.3	356
Meal, coarse, bolted	12	9.3	4.0	73.5	1.4	1.2	360
Meal, fine, bolted and degerminated	12	8.4	1.2	77.8	0.5	0.6	363
Barley							
Whole seed, except hulls, and groats	12	11	1.8	73.4	3.4	1.8	332
Pearled, light or dark	12	9	1.4	76.5	0.8	1.1	346
Oats							
Oatmeal, rolled oats	10	13	7.5	67.8	1.9	1.7	385
Sorghum							
Sorghum (*Sorghum vulgare*)	11	10.1	3.3	73.8	1.7	1.8	343
Millet							
Ragi (*Eleusine coracana*)	11	6.5	1.7	78.0	2.6	28	332
Foxtail (*Setaria italica*)	11	9.8	3.0	74.7	2.0	1.5	343
Proso (*Panicum miliaceum*)	11	11.8	2.4	72.8	2.2	2.0	338
Pearl or bajra (*Pennisetum glaucum)*	11	11.7	4.7	70.5	1.9	2.1	348
Unspecified millets	11	9.7	3.0	74.1	2.7	2.2	340

Barley

Of the various cereals, barley (*Hordeum vulgare*) has been adapted to the widest variety of climates, from sub-Arctic to sub-tropical. Barley is grown on widely in Russia, Australia, Germany, Turkey, and North America. Approximately 124 million tons of barley is produced worldwide accounting for 5% of the total cereal production and 7% of the total area harvested for the year 2010 (Table 6.2). Barley provides less than 1% of total calories and protein in Africa, the continent with the larger barley consumption per capita (Table 6.1). Whole seed, except hulls, and groats, and pearled, light or dark account for 9–11% protein, <2% fat, 73–77% carbohydrates, and up to 3.4% fibre (Table 6.3). Leading world producers in 2009/2010 were the European Union (41.4%), Russia (12.0%), Ukraine (7.9%), Canada (6.4%) and Australia (5.3%)(U.S. Grains Council, 2012). Barley is classified as six-row or two-row, describing the physical arrangement of kernels on the plant. Another classification describes the beards or awns covering the kernels. Barley is grown for feed, food, or malting. Barley grown for feed is used in rations for all animal types. Barley, although grown in smaller quantities, competes with both maize and sorghum as a feed grain in the United States. The current breakdown is approximately: 76% food, seed and industrial use; 3% export use; and

22% feed and residual use (US Grains Council 2012). At present, approximately 2% of all harvested barley is used as human food, with the rest being used in animal feed and the brewing industry (Baik and Ullrich 2008). After maize and sorghum, barley is a major feed grain crop produced in the United States. Barley is grown in significant quantities in many places around the world. Like wheat in the Western world and rice in the Eastern world, barley production, because of its importance in malt beverages, is often a cultural, rather than economic phenomenon. In Europe, in particular, this has resulted in decades of subsidy of barley and malt production so that today the European Union is currently the third largest exporter of barley and malt.

Naked (*Hordeum vulgare* var. *nudum*) and hulled barley varieties share the same genetic background, except that the naked gene, nud, is expressed in the naked types. Naked barley may be two- or six-rowed, have short or long awns, vary in straw height, and occur in hooded (awnless)-type barley. Environmental growing conditions have major influences on kernel size and composition, but kernel size and shape are also genetically controlled characteristics (Newman and Newman 2005). High-amylose and waxy hulless barley contains approximately 7 or 8% β-glucans, whereas regular hulless barley includes significantly less (4.6%) (Gao and others 2009). Together with arabinoxylans, a fraction of partly soluble non-starch polysaccharides occurring in the cell walls, β-glucan has a great impact on cereal processing and product properties. The positive effects of cereal β-glucans have been recently reviewed by Wood (2010), with most of the data deriving from studies with oat β-glucans, followed by barley and rye. The mode of action of barley β-glucan in particular included the short-time blood sugar regulating effects of bread (Vitaglione and others 2009) and of chapatis (Thondre and Henry 2009), and beneficial effects on weight management by increasing satiety (Nilsson and others 2010) and on serum cholesterol levels (Talati and others 2009). Kinner and others (2011) have compiled the health promoting legal status of ß-glucans. In 2005, the US Food and Drug Administration (FDA) concluded that a cause and effect relationship between the consumption of β-glucan and coronary heart disease lowering properties exists (21CFR101.81). In Europe, the European Food Safety Authority (EFSA) has indicated that it will allow claiming "regular consumption of β-glucans contributes to maintenance of normal blood cholesterol concentrations" (EFSA 2009) by assuming that barley β-glucans have the same effects as oat β-glucans. In order to bear the claim, EFSA demands a quantity in food of at least 3 g/day of β-glucans from oats, oat bran, barley, barley bran, or from mixtures of non-processed or minimally processed ß-glucans in one or more servings. The positive effects of β-glucans are mainly attributed to its high viscosity in aqueous solution and thus increasing the viscosity of the contents within the intestinal tract (Jalili and others 2000). Viscosity in the small intestine is determined by the concentration, molecular weight, and solubility of β-glucan. At the moment, neither FDA nor EFSA substantiate their claims on the physicochemical properties. However, on a daily dosage of 3 g/day, scientific evidence unequivocally links the effects of β-glucan with its viscosity (Wolever and others 2010), which is indirectly decreased due to degradation of the molecular weight during food processing (Tosh and others 2008). It is anticipated, that, due to legislation, the interest of food producers and consumers in using naked barley for food purposes will increase (Kinner and others 2011).

Oat

The common oat (*Avena sativa*) is a species of cereal grain grown for its seed, which is known by the same name (usually in the plural, unlike other grains). *Avena sativa*, the principal cultivated species, is variable in growth form and has been improved by breeding and selection. Other cultivated species are the side oat *A. orientalis*, the red oat *A. byzantina*, the naked oat *A. nuda,* and the short oat *A. brevis*. Approximately 20 million tons of oat is produced worldwide accounting for < 1% of the total cereal production and 1.3% of the total area harvested for the year 2010 ([Table 6.2](#)). Across continents, Europe produced 60%, and America 26% of the total oat. Oatmeal and rolled oats account for 13% protein, 7.5% fat,68% total carbohydrates, and 2% fiber ([Table 6.3](#)). Although one of the most common uses of oats is as livestock feed, they are suitable for human consumption as oatmeal and rolled oats. The percentages of ß-glucan in the various whole oat products are: oat bran, > 5.5% and up to 23.0%; rolled oats, about 4%; and whole oat flour about 4%. After maize (corn), oats have the highest lipid content of any cereal, for example, > 10% for oats and as high as 17% for some cultivars compared to about 2–3% for wheat and most other cereals. The polar lipid content of oats (about 8–17% glycolipid and 10–20% phospholipid or a total of about 33%) is greater than that of other cereals, since much of the lipid fraction is contained within the endosperm.

Sorghum

Sorghum (*Sorghum vulgare*) is one of the most drought-tolerant cereal crops currently under cultivation. As a continent, Africa and America are the largest producers of sorghum with approximately 21 and 23 million metric tons produced annually, respectively. Leading producers around the world during the fiscal year 2010 included Nigeria (11.5 million metric tons), the United States (9.7 million metric tons), India (6.98 million metric tons), and Mexico (6.25 million metric tons). Sorghum grain is the third most important cereal crop grown in the United States and the fifth most important cereal crop grown in the world. It is a leading cereal grain produced in Africa and is an important food source in India. Leading exporters are the United States, Australia, and Argentina (US Grains Council 2012).

In many parts of the world sorghum has traditionally been used in food products and various food items; porridge, unleavened bread, cookies, cakes, couscous and malted beverages are made from this versatile grain. Traditional food preparation of sorghum is quite varied. Boiled sorghums are one of the simplest uses and small, maize grains are normally desired for this type of food product. The whole grain may be ground into flour or decorticated before grinding to produce either a fine particle product or flour, which is then used in various traditional foods. Sorghum has unique properties that make it well suited for use in food. Some sorghum varieties are rich in antioxidants and all sorghum varieties are gluten-free, an attractive alternative for people with a wheat allergy. Research has shown, however, that sorghum may be used to produce a number of different food products including breads (Schober and others 2005, 2007), tortilla chips (Rooney and Waniska 2000), tortillas (Fernholz 2008), cookies (Morad and others 1984), flat breads (Badi and others 1990), and noodles (Kunetz and others 1997; Miche and others 1977; Suhendro and others 2000; Liu and others 2012). Because of its neutral taste, sorghum absorbs other flavors well. It is anticipated that more white sorghum-based products will debut soon both in Japan and in North America. Sorghum is also an important animal feed used in countries such as the United States, Mexico, South America, and Australia. Good-quality sorghums are available with a nutritional feeding value that is equivalent to that of maize. Sorghum can be processed

further to improve its feed value and techniques such as grinding, crushing, steaming, steam flaking, popping, and extruding have all been used. As much as 30–40% of domestic sorghum production goes to produce ethanol and its various co-products. With demand for renewable fuel sources increasing, demand for co-products like sorghum-distiller's dried grains with solubles will increase as well due to sorghum's favorable nutrition profile (US Grain Council 2012).

Bakery products from coarse grains: challenges and opportunities of composite breads

As the core of human nutrition, grains are ubiquitous and multifaceted staple foods presented to the population worldwide either as a carrier of macro- and micronutrients or as tailored foods for specific targeted groups as healthy, convenient, and indulgent raw materials providing perfect vectors for diversity and innovation. It raises a great deal of recent interest that minor cereals, ancient crops, and pseudocereals, besides wheat, constitute highly nutritional grains with potential bread making applications. The general growing demand for novel, tasty, and healthy foods, together with the increasing number of people that have wheat-related diseases, have given birth to a new market consisting of cereal products made from grains other than wheat and rye. As stated by Liu and others (2012), the recent increase in the wheat-free food market has been due to an increased awareness and diagnosis of celiac disease (Collin and others 2002), gluten sensitivity (Goldstein and Underhill 2001), and wheat allergies (Poole and others 2006). In this context, the challenges and opportunities of non-wheat cereals (maize, barley, oat, sorghum, and millet), pseudocereals (quinoa, amaranth, and buckwheat) and Andean crops in bread making applications deserve special attention due to their unique nutritional components – dietary fibre, resistant starch, minerals, vitamins, bioactive compounds – (Skrabanja and others 2001; Kim and others 2004; Angioloni and Collar 2011a). Angioloni and Collar (2011b) assessed the suitability of associated mixtures of minor/ancient cereals (rye, oat, Kamut wheat, spelt wheat) and pseudocereals (buckwheat) in the highly replaced matrices of multigrain wheat flour. A quaternary blend of oat, rye, buckwheat, and common wheat flours (20 : 20 : 20 : 40 w/w/w/w) without any additives and/or technological aids in the formulation was proposed to make highly nutritious, modern and innovative baked goods meeting functional and sensory standards in terms of nutritional added value, palatability, convenience, and easy handling during processing.

In bread making applications, the lack of gluten proteins to meet dough viscoelastic and fermentative restrictions has generally constrained the incorporation of substantial amounts of these underused cereals into wheat dough systems to achieve dietary and health-endorsing effects. High levels of grains other than wheat incorporated into baked products are cost effective and nutritionally advantageous, even though it is technologically very challenging. Recently, the potential ability of oat, millet, and sorghum, with a low bread making profile but potential nutritional added value (high mineral content, low digestible starch, high viscous fiber content, source of antioxidants), has been assessed in mixed matrices with common wheat, to successfully make modern and innovative fermented baked goods meeting viscoelastic and sensory standards (Angioloni and Collar 2013). Updated challenges and opportunities for maize, barley, oat, sorghum, and millet in bread making applications are revised, and recent achievements highlighted in this section.

Maize breads

Broa, the Portuguese ethnic bread, is made empirically with more than 50% of maize mixed with wheat or rye flours, and is highly consumed in the north and central zones of Portugal. Few scientific studies on broa bread making have been reported, since research has mainly

focused on the partial replacement of wheat flour by maize flour (Martìnez and el-Dahs 1993) or maize starch (Miyazaki and Morita 2005) or developing formulations based on maize starch (Sanni and others 1998; Özboy 2002). The impact of different factors such as maize variety, type of milling, and water mixing temperature on maize dough rheology to define and optimize maize bread making in gluten-free broa has recently been assessed (Brites and others 2010). Maize-based gluten-free breads were obtained following the broa bread making process, and produced bread with satisfactory sensory characteristics and a similar appearance to traditional broa.

Maize processing produces large quantities of defatted maize germ (DMG), digestible and resistant starch with potential bread making applications. The use of DMG, nutrient-rich by-product (high protein content with a protein efficiency ratio value comparable to that of soy protein, and richer and more balanced in most of the essential amino acids than wheat flour) in bread making has been investigated, and results demonstrated that acceptable physicochemical and sensory quality bread could be made with the addition of DMG flour at 15 g/100 g wheat flour (Siddiq and others 2009). It has been reported that the addition of maize resistant starch to bread (maize, wheat, and rye flours) significantly decreases the glycemic curve, typically reversing the insulinogenic effect of the carbohydrate content of wheat bread and is associated with decreased serum cholesterol levels (Brites and others 2011). This suggests the interesting possibility for formulating foods that have a high frequency of consumption, such as bread, with nutrition and health claim labeling. Utilization of the most representative Portuguese bread formulation (broa) and baking process was a salient feature of the study, reporting for the first time a comparison between postprandial glucose responses after the ingestion of wheat and maize breads. The authors suggest that nutritional and health claims can be made for resistant starch-enriched breads; for maize bread, for example, a nutritional claim statement could be "naturally increased resistant starch content" accompanied by the health claim "naturally low glycemic index." Heat-moisture-treated (HMT) starch – a modified starch obtained by heating at 90–100 °C for more than 16 h under vapor pressure – has proven to greatly change its physicochemical properties; gelatinization temperature, water-binding capacity, and enzyme susceptibility increased with treatment, and viscograph consistencies and swelling powers decreased with increasing moisture content during heat treatment (Kulp and Lorenz 1981). A bread making application using 20% replacement of wheat flour showed no significant improvement of baking performance despite formula enrichment (Miyazaki and Morita 2005). Further studies are encouraged to modify baking methods and ingredients for the practical application of HMT starch in bread making.

Barley breads

The beneficial health effects of ß-glucan, a major non-starch polysaccharide in barley, have become the focus of much attention in recent years, with the incorporation of barley fractions into baked products being a growing area in the development of healthier food products. Despite the numerous health promoting properties of naked barley associated with its high levels of ß-glucans, barley flour is currently hardly used for human consumption. In addition to the poor baking properties of naked barley that lacks a gluten network, the high concentration of ß-glucan decreases water availability for the protein network and thus impairs baking properties (Gill and others 2002). Thus, the maximum level of barley flour

recommended was 10% based on flour for yeast leavened breads (Bhatty 1986). As a compromise between sensory attractiveness and additional health promoting benefits, barley flours substituted other flours at a maximum of equal parts in a study by Cavallero and others (2002), although usual levels range from 15 to 20% (Skrbic and others 2009). An optimized formulation for bread based on 100% naked barley flour has recently been developed (Kinner and others 2011). For this, an experimental design and statistical multiple response optimization was used to obtain a dough with technologically feasible processing properties and bread with satisfying sensory attributes containing sufficient ß-glucan to increase the daily intake and to be in accordance with the scientific opinion of EFSA (Kinner and others 2011). In another study, flour formulations, doughs, and breads were produced using the "middling" fraction of wholegrain and pearled barley in different ratios (15%, 30%, 45%, and 60% middlings with wheat flour). A 100% wheat formulation was used as a control. Bread quality was not significantly affected by the addition of up to 30% barley middling, the loaf volume and textural properties in particular of breads up to 30% barley middling inclusion were of a suitable standard when compared to the control. Both fiber and ß-glucan content of the breads were increased significantly with the inclusion of barley middling; inclusion of barley middling at a 30% level increased the fiber and ß-glucan contents, respectively (Sullivan and others 2011). The incorporation of 40% barley to wheat flours increased the antioxidant properties of the breads compared to the control bread, and a good consistency between the sensory evaluation and the amount of phenolics was found (Holtekjølen and others 2008). The combined use of hull-less barley flour and xylanase was a plausible strategy to increase arabinoxylan and ß-glucan levels in barley/wheat (40/60, w/w) composite breads (Trogh and others 2004). Supplemented wheat breads with hull-less barley flour and flakes had high fiber, zinc, and selenium contents. It was estimated that a 300 g daily portion of such breads could meet up to 40% of dietary recommended intakes for selenium and 70–75% of recommended daily values for ß-glucan without a significant deterioration of sensory acceptability (Škribic´ and others 2009). Pita bread made from fortification of wheat flour with barley flour and barley protein isolate at 15% exhibited superior chemical, physicochemical, nutritional, and biological properties in terms of increased contents of essential limiting amino acids, total phenolics, antioxidant activity, and inhibitory activity for both angiotensin converting enzyme and α-amylase (Alu'datt and others 2012). The potential of sourdough to improve the bread quality of barley- and oat-enriched wheat breads may depend on the characteristics of the added flour (cereal type, variety, extraction rate). The effect of different barley flours and oat bran (substitution level 40%), unfermented and as sourdoughs (20% of total flour), on composite wheat dough and bread characteristics were compared by combining empirical rheological with small-scale baking of hearth loaves. Whole grain barley flour sourdough improved the form ratio of hearth loaves compared to unfermented whole grain barley flour. However, sourdough showed little effect on the breads prepared with sifted barley flour or oat bran (Rieder and others 2012).

Oat breads

Oat (*Avena sativa*) is one of the most adventurous cereal grains for the human diet since it contains naturally high amounts of valuable nutrients such as soluble fibers, proteins, unsaturated fatty acids, vitamins, minerals, and phytochemicals (Flander and others 2008). Bread made from oats not only has a high nutritional quality, but it is also considered to have

a nutty, mild, and pleasant aroma (Flander and others 2007) and excellent moisture retention properties that keep the bread fresher for longer (McKechnie 1983). The use of oats in baking could therefore improve the nutritional quality of bread considerably. Oats are a health promoting cereal crop with nutritional advantages including high lipid and β-glucan concentrations and a low starch content compared with other cereal grains. Some physiological responses have been linked to the intake of oat products, mainly due to the high concentration of ß-glucans (Wood 2007): (i) a small reduction of serum cholesterol levels in people with elevated cholesterol levels; and(ii) an attenuation of the postprandial glycemic response. The intake of approximately 3.2 g of ß-glucan per day is capable of lowering cholesterol from −0.13 to −0.16 mmol/l (Truswell 2002). The addition of more than 20 g oat/100 g wheat flour into bread formulations usually lead to tight, highly moist, and gummy unacceptable breads. Flander and others (2007) obtained acceptable oat–wheat breads (51 : 49, w : w) after recipe optimization by adding a surplus of water (91.5/100 g flour) and a high amount of gluten (15.2/100 g flour). Oat proteins do not possess the unique viscoelastic properties characteristic for wheat gluten, resulting in lower quality products, that is lower bread volume. The effects of oats on dough properties and bread quality have therefore been studied mainly on composite breads made from wheat and oats, with addition levels ranging from 10 to 60% of oatbran, flakes, or flour (D'Appolonia and Youngs 1978; Zhang and others 1998; Degutyte-Fomis and others 2002; Flander and others 2007, 2008; Angioloni and Collar 2013). In these studies, the bread making properties of oats were masked by the outstanding effect of wheat gluten and little work has been carried out to examine the bread making properties of oats without the addition of wheat or structure forming agents (Angioloni and Collar 2012). Breads made from oats without added wheat require a different technology, as they are more fluid than wheat doughs and closer in viscosity to cake batters (Schober and others 2005). Small flour particle size, damaged starch granules, and high protein content were identified as the key factors causing the increased water hydration capacity. Oat flours with coarse particle size, limited starch damage, and low protein content resulted in superior oat bread quality (Hüttner and others 2010). The use of an optimized sourdough process in the production of oat bread provides a feasible technology for producing new tasty variants of oat bread with a high ß-glucan content (Flander and others 2011). One portion (two slices of 25 g) of this bread contained 0.8 g ß-glucan. Additionally, the combination of wheat sourdough and oat could be a potentially reduce the GI of wheat bread (De Angelis and others 2007). The amount of sourdough added and its fermentation temperature had significant effects on the texture and crumb characteristics of the oat–wheat bread. The most favorable sourdough condition for enhanced crumb texture and flavour of the bread was a small addition of wheat sourdough (10 g/100 g dough) that was fermented at 40 °C for 20 h. The use of optimized sourdough resulted in bread with a similar specific volume and staling rate than the corresponding straight dough bread. Wheat sourdough did not affect the content or average molecular weight of the ß-glucan when compared to straight dough bread. The molecular weight of the ß-glucan decreased slightly, and to the same extent in both breads, when compared to the oat flour. The degradation of the ß-glucan occurred during the bread making phase, and was most likely due to the endogenous ß-glucanase activity present in the wheat flour.

Sorghum breads

Sorghum has certain physicochemical properties which negatively affect its technological

properties (Onyango and others 2011). Flour from the horny endosperm gives coarse grits on milling which contribute to the coarse, gritty or sandy mouth feeling (Schober 2009). Upon cooking, sorghum proteins form extended web- or sheet-like structures with embedded starch (Hamaker and Bugusu 2003). The protein aggregates may affect various technological properties of sorghum. Schober and others (2007) found that sorghum proteins in the liquid phase of the batter aggregate during baking to form strands and lumps which interfere with the starch gel, resulting in bread with a flat top and holes in the crumb. The endosperm and bran particles deform and puncture the gas bubbles in the batter, causing leakages and rigid brick-like bread with a low volume. The high gelatinization temperature of sorghum may cause inadequate gelatinization during baking leading to undesirable white streaks and patches on the crust surface and a coarse mouth feeling (Taylor and Belton 2002; Schober 2009). A recent paper by Yousif and others (2012) reported that the incorporation of wholegrain sorghum flour into refined wheat flat breads did not dramatically modify either their proximate and dietary fiber composition or its sensory acceptability compared to the refined wheat control. The lower levels of rapid digestible starch in the sorghum flat breads suggest that incorporation of whole-grain sorghum flour into refined wheat flour flat bread may have the potential to lower its effect on post-meal blood glucose levels in humans. This would provide a low glycemic index food product of benefit for the long-term protection from type 2 diabetes mellitus. In addition, the increased polyphenolic levels and antioxidant capacity of the breads containing sorghum may provide protection from oxidative stress and hence reduce the risk of chronic diseases, such as type 2 diabetes mellitus, cardiovascular disease, and some cancers. Angioloni and Collar (2013) found that up to 30% of wheat flour replacement by sorghum can be incorporated into the binary blended matrices with minimal techno-functional impairment and sensory depreciation of blended breads. Combinations of gluten, vegetable fat, and a commercial mix of surfactants, ascorbic acid, and antistaling enzymes were used successfully to make high scored breads with a 10% increased level of wheat flour replacement by sorghum in binary mixed samples. Sorghum, like legume and oil seed meal, has some limitations due to the presence of antinutritional factors, such as trypsin and amylase inhibitors, phytic acid, and tannins, which are known to interfere with protein and carbohydrate digestion and mineral bioavailability. Reduction or elimination of these undesirable components is essential for improving the nutritional quality of sorghum and effectively utilizing their full potential as human food. Fermentation has been used to improve the nutritional quality of sorghum through mobilization of nutrients and reduction of the antinutritional content in cereal. Chavan and others (1988) reported that fermentation of sorghum increased protein content, soluble protein, and free amino acids. Similarly, Kazanas and Fields (1981) found an increase in essential amino acids and the nutritive value of sorghum during natural fermentation. Trypsin inhibitor activity, phytate phosphorus, and flatus sugars were significantly decreased when maize and maize–soy blends fermented for 4 days (Chompreeda and Fields 1981). Reddy and Salunkhe (1980) reported almost complete elimination of phytate phosphorus within 8 h fermentation in rice. Natural fermentation of sorghum has also been found to reduce tannin content and improve *in vitro* protein digestibility (Yousif and El-Tinay 2001). In Saudi Arabia, grain sorghum is used in the Gizan region for making a fermented bread called Khamir, utilizing the natural microflora in sorghum flour (Gassem 1998). Traditional fermentation of the local sorghum varieties resulted in a significant reduction of trypsin and amylase inhibitory activities, phytic acid, and tannin. Fermentation was also found to significantly improve *in vitro* protein digestibility. These results clearly indicate that fermentation may be useful for improving the nutritional

quality of sorghum with respect to protein and carbohydrate utilization as well as mineral bioavailability (Osman 2004). Sorghum is a good source of phenolic compounds with a variety of genetically dependent types and levels including phenolic acids, flavonoids, and condensed tannins. Pigmented sorghums contain unique anthocyanins that could be potential food colorants. These tannin sorghums are excellent antioxidants, which slow hydrolysis in foods, produce naturally dark-colored products, and increase the dietary fiber levels of food products. Sorghums have a high concentration of 3-deoxyanthocyanins (that is, luteolinidin and apigenidin) that give stable pigments at high pH. Pigmented and tannin sorghum varieties have high antioxidant levels that are comparable to fruits and vegetables. Finger millet has tannins in some varieties that contain a red testa. There are limited data on the phenolic compounds in millets; only phenolic acids and flavones have been identified (Taylor and Dewar 2000; Dykes and Rooney 2006). The literature is relatively scarce compared to that of maize and rice in exploring sorghum for production of foods for Western markets. Recently, in the United States, sorghum hybrids that produce white grain from a tan plant (often called "food grade" sorghum) were used for the production of wheat-free foods for persons with celiac disease. The development of white food-grade sorghum lines means that white, neutral tasting flour can be produced from sorghum. These flours are useful in food products because they do not impart unusual colors or strong flavors and favored over maize flours for these reasons. Sorghum protein digests did not elicit any morphometric or immunomediated alteration of duodenal explants from celiac patients. Sorghum-derived products did not show toxicity for celiac patients in both *in vitro* and *in vivo* challenge. Therefore sorghum can be considered safe for people with celiac disease (Ciacci and others 2007).

The production of bread, cakes, pasta, and cookies from sorghum is being widely investigated for several reasons: (a) sorghum is considered a safe alternative to wheat for celiacs, (b) there is a need to find local alternatives to wheat for bread making in tropical countries where wheat cannot be grown (Taylor and others 2006; Schober and Bean 2008), and (c) sorghum has a considerable amount of phytochemicals, particularly polyphenols, with high antioxidant activity. The production of good-quality non-wheat bread with a light, airy texture is still a challenge. The general principle of successful non-wheat bread making is that the solute molecules in the dough, mainly starch, have to substitute for the gas-holding, viscoelastic properties of the wheat gluten molecules (Taylor and Anyango 2012). Specifically, the solute molecules have to interact together with the water molecules to hold the gas produced during yeast fermentation, allowing the dough to expand during fermentation and to set into a firm cellular structure during baking. In this context, sorghum has no special characteristics compared to other gluten-free cereals such as maize or rice. However, the more bland taste of white, tan-plant sorghum cultivars compared to other cereals and other sorghum types seems to be preferred in bread and cakes. The lack of viscoelastic proteins in hydrated sorghum flours leads to specific requirements in sorghum doughs for bread making: much higher hydration (80–110%) and addition of 30% of starch relative to flour (Schober and Bean 2008). These special conditions allow greater starch granule expansion during baking, favoring the formation of a more stable gas cell structure. In addition, hydrocolloids such as xanthan gum and hydroxypropylmethylcellulose or pregelatinized starch are commonly added to the formulation to increase the viscosity of the aqueous phase of the dough so as to reduce the rate of gas loss from the dough (Taylor and others 2006). Despite formula optimization, sorghum breads have a coarser crumb structure, with proportionally larger gas

cells and thicker cell walls. Gluten-free cakes and muffins more closely resemble their wheat flour counterparts, probably because the role of gluten is not crucial in cake making. The flour has a much lower proportion of the solutes because there are high levels of sugar and fat, and eggs are generally included (Taylor and others 2006), which all play a role in gas cell stabilization. Cookies (biscuits) are easily made from sorghum flour (Chiremba and others 2009; Taylor and others 2006) because unlike bread and cakes, they are not leavened. No special ingredients are required. However, sorghum cookies tend to be denser and have a harder texture than their wheat counterparts and can have a somewhat gritty mouthfeel (Chiremba and others 2009).

Millet breads

Finger millet or ragi (*Eleusine coracana*) is the principal dry land crop for many peoples in East Africa and South-East Asia (Raghu and Bhattacharya 2010). Finger millet, rich in calcium and dietary fiber, is extensively consumed by the South Indian rural population and is used both in the native and the processed (malted) forms (SubbaRao and Muralikrishna 2001). Although finger millet does not enter the international markets as an item of trade, it is an important crop in the areas of adaptation, and is a good source of protein, fat, and phytochemicals such as polyphenols, dietary fiber, and minerals (Chethan and Malleshi 2007). Some health benefits associated with the regular intake of millet foods – such as its hypocholesterolemic, hypoglycemic, and antiulcerative characteristics – indicate the scope for its use by non-traditional millet consumers (Shobana and Malleshi 2007). Hence, providing millet in a similar way to rice or wheat or as a ready-to-eat convenience cereal would improve its acceptability. It has recently been incorporated during the preparation of various biscuit. It is usually converted into flour and made into products such as pudding, porridge, and pancake. Several studies indicated the possibilities of incorporating millet and other flour in wheat flour at various levels for producing bread, biscuits, and other snacks (Saha and others 2011). Millet can provide a sustaining diet. Malted finger millet is used as a nourishing food for infants, and it is considered as a wholesome food for people with diabetes (SubbaRao and others 2004). Recently, the optimum conditions suitable for developing a flattened product and bread spread have been computed. Enzymatic treatment with bacterial α-amylase is an option to modify the attributes of finger millet flour dough related to processing and product development (Raghu and Bhattacharya 2010). In the presence of wheat flour, millet flour led gave composite bread matrices with acceptable sensory and enhanced nutritional qualities (Angioloni and Collar 2013, 2012).

Conclusions and future prospects

Exploitation of non-gluten forming cereals such as maize, oat, barley, sorghum, and millet in food is still mainly limited to ethnic goods. Bread making applications are constrained for several reasons: (i) the lack of endogenous viscoelastic proteins giving semipermeable dough systems mandatory in leavened bread production; (ii) difficulties in properly mimicking the gas retention capability of the gluten network in wheat matrices; and (iii) the need of structural agents and/or expensive additives to restore dough viscoelasticity. In-depth research is needed to determine how to enable the non-gluten forming cereal proteins to provide dough viscoelasticity to bread systems. In addition, retention of micronutrients must be improved and knowledge of endogenous phytochemicals needs to be extended. Composite flours have proven to offer a viable alternative to enhance dough viscoelasticity in mixed matrices that include wheat flour. Optimization of both the qualitative and quantitative composition of mixed matrices and the adequacy of specific processes of individual cereals will play an integral role in cost savings, promoting the worldwide use of local crops with high nutritional value and enhancing the agricultural systems in countries producingthese cereals. Advances in nutrition and technology in the application of coarse cereal grains are expected to progress as their health-promoting effects accumulate and are endorsed by international health authorities.

Acknowledgments

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Part 3
Baking Ingredients

7

Water[a]

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Introduction

The importance of water as a baking ingredient is overshadowed by its overwhelming abundance. The role of water in baking science is perhaps underrated or neglected by most of us, but all master bakers know that water plays a major role in the art and science of baking. The amount of water controls the quality, texture, taste, smell, volume, flavor, and mouth feel of bakery products. The art of baking includes the use of optimum quantities of quality water (Cauvain and Young 2000).

Life originated in water, and all life forms continue to require water to help them digest and utilize food. Water provides a medium in which biochemical reactions take place for growth and multiplication. What is water and why is it so essential to life? Humans continue seeking answers to this question even though we already have some answers.

Some animals drink water directly, whereas others get their water from food. Nearly all foods contain water, which is the major component in many foods. Even dry foods contain some percentage of water. If the baking process does not call for water as an ingredient, water is still involved, because it is present in some of the ingredients. Water reacts with baking ingredients and evaporates when heated.

Water

Water is a compound of hydrogen (H) and oxygen (O), and is generally represented by the chemical formula H_2O. Both hydrogen and oxygen have isotopes, but this formula is used to include all isotopic water molecules.

Baking sciences need not consider isotopic composition. However, it is interesting to point out that a significant amount of heavy water has been extracted from water for nuclear technology and for research in the life sciences. *Deuterium* (D or ^2H) atoms replace hydrogen atoms in heavy water, whose formula is D_2O or ^2H_2O. Properties of heavy water differ from those of H_2O, and the difference, called the *isotopic effect*, is also present between H and tritium (T or ^3H). *Tritium* is a radioactive isotope of hydrogen, and T-containing water is radioactive. Radioactive and heavy waters may be applied to research in bakery, but their presence in food at levels higher than those in natural waters are undesirable, due to their adverse effects.

Strictly speaking, water is the liquid state of the natural compound H_2O, but the compound exists in solid, liquid, and gaseous states at conditions on earth's surface. All three states and their transformation are involved in bakery products and baking processes. Thus, the term *water* should be taken in this chapter to mean the compound water in any of its three states.

For reasons given later, water molecules are present in food as well as in many other substances. Due to the strong interactions between molecules of water and those of other substances, the properties of water molecules interacting with other substances will be dramatically different from those of pure water. Although water is a natural resource, "natural waters" are not pure: they contain dissolved minerals and gases at different concentrations. In scientific terms, natural waters are solutions, but because they are very dilute, they are generally considered natural waters, or simply water.

Drinking water

Not only the water in beverages, but all waters used in food production, washing, processing, and baking are called *drinking waters*. The Handbook of Drinking Water Quality (De Zuane 1997) sets guidelines for waters used in baking. Wastewater from the baking industries needs treatment, and the technology is usually dealt with in industrial chemistry (Lacy 1992).

The U.S. Environmental Protection Agency has a website (www.epa.gov/safewater/) devoted to safe drinking water. It covers the basics of water and health, drinking water standards, local water information, water databases, the safe drinking water act, water infrastructure security, water information for children, and water in the news. The EPA develops and oversees the implementation and enforcement of regulations for drinking waters provided by public water systems. Bottled water is considered a food and is therefore regulated by the U.S. Food and Drug Administration (FDA). In 1978, the FDA adopted the EPA drinking water standards for bottled water.

Treatments for drinking water

Drinking water sources can be wells, springs, lakes, rivers, seas, the ocean, or a combination

of these. Depending on environmental and weather conditions, natural waters are usually treated to produce drinking water.

Drinking water is a very complicated issue, as we shall see from the various regulations, standards, policies, and guidelines. Since guidelines and standards are available from various sources and they vary from region to region, a commonsense technical summary for treatments of drinking water is outlined here.

Physically and aesthetically, all solids, colors, odors, and tastes must be removed for drinking water. Currently, there is a lack of public confidence in drinking water systems. The bottled-water industries flourish partly because they offer aesthetically pleasing and convenient packages.

Biologically, the water should be free of harmful microorganisms. Microorganisms thrive in waters containing organic waste. Special attention should be given to conditions that allow organisms to multiply. To detect every organism is very difficult, and often indicator organisms such as total coliforms, fecal coliforms, and *E. coli*, are tested because they have similar needs to those of pathogenic bacteria (Percival et al. 2000). Disinfection can be achieved by using chlorine, ozone, UV radiation, or gamma ray radiation, among others, and the choices depend on the circumstances. The biology of the water is often indicative of water quality, but some plants and animals in the environment also produce toxins.

Chemically, certain metal ions and anions should be below safe limits. Toxic organic and inorganic chemicals dissolved in water from the environment should be monitored so that they will not post a danger to short- or long-term health. It is very costly and impractical to continuously test for all chemicals, but some common ones, especially carcinogens and dioxins, must be checked often, and accumulative chemicals such as mercury and lead deserve special attention. The chemistry of hard water and principles for osmosis water treatment are described later in this chapter.

Radioactive contaminants are rare. Radioactive contamination occurs near nuclear reactors or after nuclear accidents. These contaminants, however, can be easily monitored with radioactivity detectors. A knowledge base exists to identify specific radio-nuclides and trace their sources.

An effective infrastructure or system is required to prevent accidents. The system should take the human factor into consideration to cover testing, monitoring, reporting, actions taken, and accountability. High priority should be given to high-risk issues.

Laboratories in local water supply authorities test water sources and provide proper treatment to produce drinking waters, and these facilities also monitor treated drinking waters regularly to make sure the waters leaving the water plants meet the standards. When unsafe waters get into the public system, the authorities have the obligation to advise the public and/or supply alternative sources of drinking water.

If a bakery industry is located outside a major city, it may have a private source of water. Although government agencies may or may not have authority over the water a company uses, the company is fully responsible for the safety of the water.

Aside from the EPA and FDA, the National Center for Infectious Diseases, the National Center for Environmental Health, the National Institutes of Health, the Centers for Disease Control and Prevention (CDC), and the U.S. Office of Water Quality, the American Water

Works Association, the Water Quality Association, and the Geological Survey are all involved with water supply and water quality. Furthermore, states and municipalities have water authorities and committees to oversee local water systems. In this regard, the situations in Canada and in other developed countries are similar.

The U.S. clean water act

For the protection of the surface water quality, the United States passed the Federal Water Pollution Control Act, widely known as the *Clean Water Act* (CWA), in 1972. Since then, regulatory and nonregulatory measures have been introduced to reduce pollutants discharged into the waterways. The EPA has the authority to implement pollution control programs and to set quality standards for all contaminants in surface waters. Many amendments have since been implemented. A 30th anniversary snapshot of the law in the electronic version, dated 2002, can be found on the EPA website: epa.gov/r5water/cwa.htm.

The purpose of the act was to restore and maintain the chemical, physical, and biological integrity of waters for the propagation of the wildlife that ensure the continuation of human existence. At the start, the EPA, the states, and Indian tribes focused mainly on the chemical aspects of water quality. Slowly, the physical and biological health of the waters began to be stressed. Furthermore, restoration work is being done for impaired waters.

Most bakery industries use the drinking waters of nearby population centers and discharge their wastewaters into the municipalities' sewage treatment plants. As long as the discharge is acceptable to the affected communities, this is less complicated than the bakeries having their own sources of water and treating their own wastewaters. However, due to the excessive organic matter present in the wastewaters, municipalities may impose a surcharge for bakeries.

Water quality and health in canada

In May 2000, heavy rain brought surface water from a nearby farm into one of three water wells, and the failure of a chlorination device led to the distribution of water contaminated with *E. coli* O157:H7 and *Campylobacter jejuni* to Walkerton, Ontario, Canada, population 4800. Half (2300) of the population became ill, many seriously, and seven died. Following a public inquiry into the tragedy, more than 90 recommendations were given. Hence, the Ontario government added new drinking water regulations to its Water Resource Act. The updated and strengthened Ontario Drinking Water Standards became law. The government routinely carries out inspections of water facilities. Elimination of disease-causing organisms by disinfection became a minimum level of treatment, and laboratories must meet stringent accreditation procedures to qualify for water analysis and testing.

The Walkerton tragedy also brought a challenge to politicians, scientists, engineers, civil servants, and academics to develop new technologies for water quality monitoring, so that proper and quick actions could be taken to prevent similar incidents anywhere in the world (Brown and Hussain 2003).

In 2004, the House of Commons of Canada introduced Bill C209, the *Canadian Safe Drinking Water Act*, to ensure safety throughout Canada and to provide for the reporting of noncompliance with safety standards. The act empowers the Minister of Health to oversee and enforce the regulations. For this purpose, the Ministry establishes a Canadian Safe

Drinking Water Committee to monitor compliance with the National Standards, to undertake research regarding drinking water, and to advise the Minister on water regulations.

Health Canada, a government agency, through its branch Healthy Environments and Consumer Safety, is involved in setting drinking water standards, conducting research and development of safe drinking water technologies, and assessing drinking water treatment processes (see www.hc-sc.gc.ca/hecs-sesc/water/).

Water concerns of the world health organization (WHO)

Drinking water standards are a global concern, and the World Health Organization (WHO) naturally cares about water because it is intimately related to health. WHO provides a set of guidelines (www.who.int/water_sanitation_health/dwq/en/), and it particularly pays attention to infectious diseases carried by water. It recommends an international network to promote household water treatment and safe storage, especially in less developed areas.

WHO studies many water issues, for example, quality of water resources, recreational water use, water for crop irrigation, technology and monitoring of water sanitation, water-related disease, wastewater reuse, and others. Many WHO publications on water related to health and sanitation are available on the Internet as well, and the organization responds to emergencies anywhere in the world.

Water and baking ingredients

Water is an essential baking ingredient, and other baking ingredients may also contain water, although the quantities in the other ingredients may not be well defined. In a bakery product, all ingredients interact among one another at the molecular and atomic levels to give the final texture, flavor, taste, aroma, character, palatability, and mouthfeel. As shall be seen, water is a polar substance, and it strongly interacts with other polar ingredients. Based on their interactions with water, water-soluble polar ingredients are *hydrophilic*, whereas nonpolar ingredients are *hydrophobic*. Substances whose molecules have both polar and nonpolar parts are *amphiphilic*. These substances include detergents, proteins, aliphatic acids, alkaloids, and some amino acids. However, detailed information about the water molecule and the properties of water is needed to describe their interactions at the molecular level.

Baking ingredients are mixtures of many compounds. Each compound has its unique properties, but only the interactions of water with some of the major classes of compounds in several ingredients will be discussed here. These interactions depend on temperature. As temperature rises, Maillard reactions take place, producing various compounds in the final bakery products (Mottram 1994).

Flours, a common ingredient, contain mostly starch and proteins. *Starches* are carbohydrates, polymers of six-carbon sugars. Each six-carbon sugar unit has three hydroxyl (—OH) groups that can strongly interact with water molecules. Small starch molecules are soluble in water, whereas large ones are not. Therefore, starch is hydrophilic, but water molecules take time to get into the tightly packed starch granules. *Proteins* are polymers of amino acids; all have hydrophilic groups, but some also contain hydrophobic groups. Thus, proteins may contain hydrophobic segments. When water is added, chains of proteins mingle, forming sticky globules. Wheat flours also contain water-soluble *pentosans,* polymers of five-carbon sugars. At high temperatures, starch gelatinizes. These phenomena are all related to interactions with

water.

Sugars are added for fermentation and flavor. Brown sugar, white sugar, confectioner's sugar, syrup, honey, molasses, maple syrups, lactose, and caramel contain 12-carbon and six-carbon sugars, all hydrophilic. The small sugar molecules are much more soluble in water than starch, polymers of sugar. Liquid sugar is an aqueous solution of a blend of these sugars.

Yeast consists of single-cell microorganisms. Water helps them convert sugar into carbon dioxide and alcohols in anaerobic conditions and to water and carbon dioxide when oxygen is available. When dry, yeast becomes dormant spores, and they thrive when water and food such as sugar and minerals are available at suitable temperatures. Fermentation involves many *enzymes*, which are large protein molecules for catalyzing specific reactions.

Table salt, NaCl, is a preservative as well as a flavor agent. Baking soda, baking powder, and cream of tartar are leavening agents. These and other inorganic ingredients are *electrolytes*, because their solutions contain positive and negative ions to conduct electricity. These ions strongly attract the polar water molecules. Baking powder contains sodium bicarbonate and a dry acid (cream of tartar, phosphoric acid, or sodium aluminum sulfate), which react to give carbon dioxide only in the presence of water. Inorganic substances affect water in many ways, and minerals dissolved in natural waters affect yeast activity as well as the quality of dough and products. Ion-protein interactions will be described later in this chapter.

Esters of fatty acids belong to a group of organic compounds called *lipids*, which are hydrophobic compounds such as oil, butter, margarine, lard, tallow, and shortening. They do not mix with water, but they have special functions in bakery products. On the other hand, parts of the large or long molecules in phospholipids, glycolipids, and steroids (lipids) are hydrophilic. They are used as *emulsifiers*, and their molecules bridge hydrophilic and hydrophobic molecules in baking products.

Due to the large amount of water in milk, separate milk components are often added to bakery products for proteins or lipids. About 87% of whole milk is water. Milk is an aqueous solution of minerals, lactose, and proteins, with additional fat and protein globules suspended in it. Hydrophobic components dissolve in the milk-fat droplets, whereas hydrophilic components dissolve in water. As pH changes, caseins precipitate, leaving lactose, minerals, water-soluble proteins, and fat in the whey.

Eggs also contain a variety of components, including proteins, lipids, minerals, and 73% water. A membrane separates the egg white from the yolk. The two have different chemical compositions, with practically all lipids in the yolk, and they may serve different purpose in baking. Egg white is an aqueous solution of proteins, whereas the yolk is an emulsion of lipid, proteins, water, and minerals.

Flavor is a sensation due to many factors including compounds produced during baking. Small amounts of various spices and flavor compounds are often added to bakery products, before or after the baking process. Thousand of components are involved, and these may be hydrophilic or hydrophobic, depending on their molecular structures.

The polar water molecules

During the 20th century, the study of materials reached the atomic and molecular levels. Research in baking science began looking at chemical reactions between molecules during baking. The shapes, structures, and properties of molecules are important for understanding these reactions. Since water is involved in almost all baking processes, the shape, structure, and properties of H_2O are described here so that its interactions with other baking ingredients can be discussed.

After careful review of many recent studies, the O—H bond length and the H—O—H bond angle in the water molecule, have been given, respectively, as 95.72pm (picometer, 1pm=10~^{12}m) and 104.52° (Petrenko et al. 1999). The atomic radii of H and O are 120 and 150pm. Note that the bond length is considerably shorter than the sum of the two atomic radii. Assuming atoms have spherical shape, some water molecules are shown in Figure 7.1.
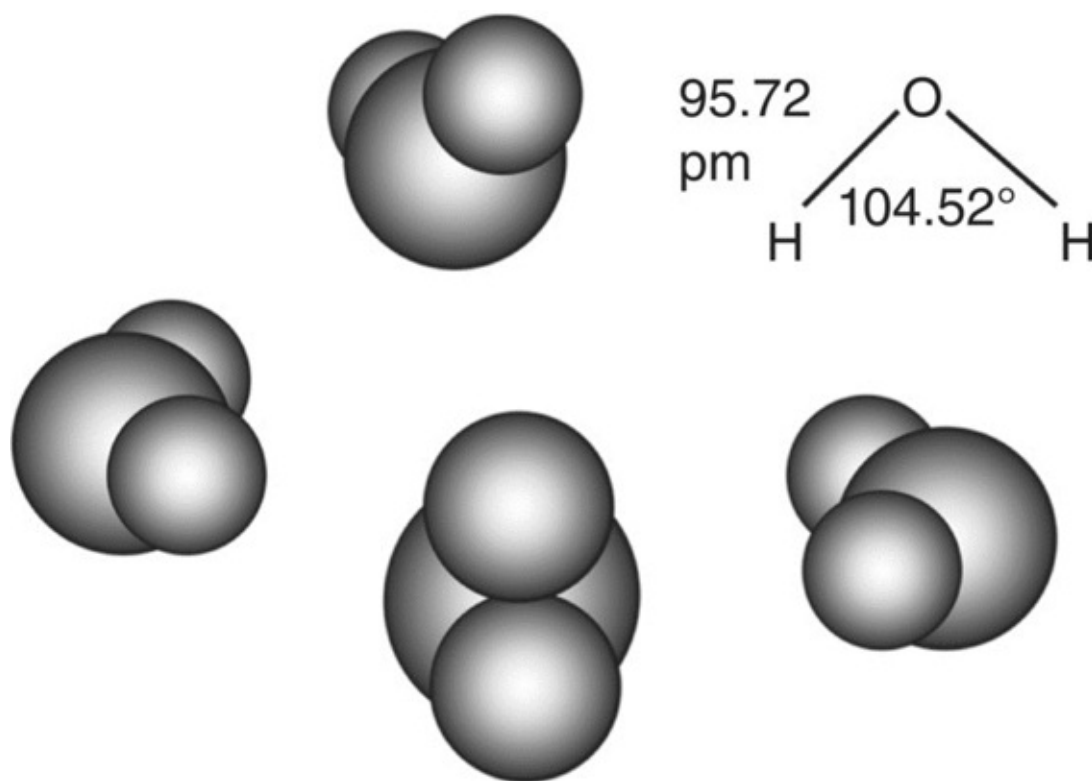
Figure 7.1 Bond length, bond angle, and some imaginary models of the water molecule, H_2O.

Most organic baking ingredients are made up of the elements H, C, N, and O. Each carbon atom forms four chemical bonds with H in CH_4. Carbon atoms bond to other carbon atoms as well as to atoms of other elements, forming chains, branched chains, rings, and complicated molecules. These carbon-containing substances are called *organic compounds*. With one and two more electrons in each N and O atom, respectively, they form NH_3 and OH_2 (same as H_2O). The extra electrons led NH_3 to have one *lone pair of electrons* and H_2O to have two lone pairs. These molecules are shown in Figure 7.2 to show their relationships.

4 shared or bonding electrons | 3 shared or bonding electrons | 2 shared or bonding electrons

Lone pair of electrons

2 lone pairs of electrons
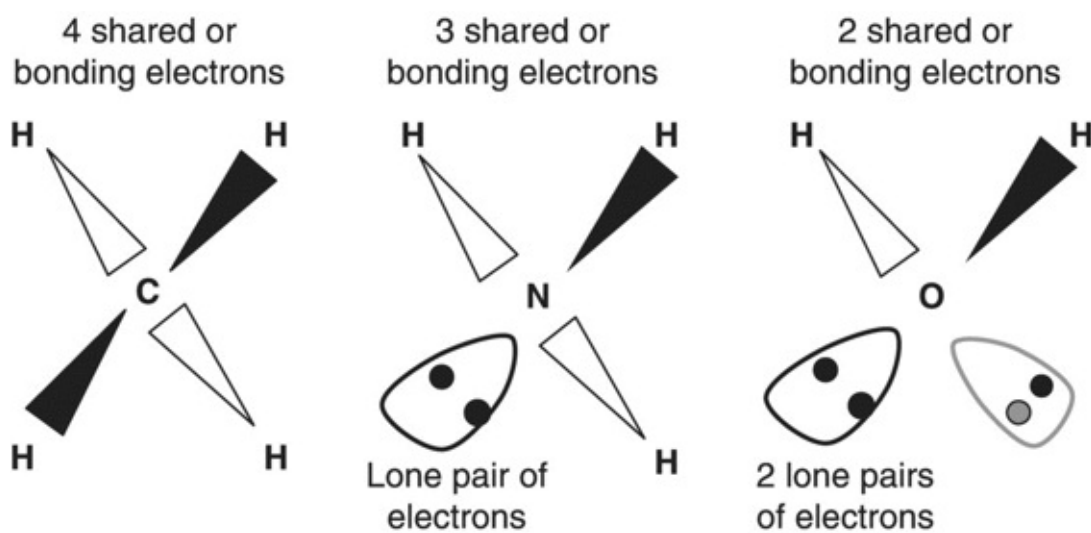
Figure 7.2 Molecules of CH4, NH3, and H_2O. A lone pair of electrons is the negative site, and it seeks the positive site of other molecules

Shared electron pairs form single bonds. The shared and lone pairs dispose themselves in space around the central atom symmetrically, or slightly distorted when they have both bonding and lone pairs.

The lone pairs are also the negative sites of the molecule, whereas the bonded H atoms are the positive sites. Before the discovery of electron, the British chemist Humphrey Davy (1778–1829) once suggested that electricity had something to do with chemistry. The discovery of protons and electrons led to the idea of charge distribution in molecules. Due to the positive and negative sites, NH_3 and H_2O are *polar molecules*. The quantity of polarity is called the *dipole moment*. The dipole moments of NH_3 and H_2O are 4.903×10^{-30}C—m (= 1.470 D) and 6.187×10^{-30}C—m (= 1.855 D), respectively. Their large dipole moments contribute to their unique interactions with baking ingredients.

Gaseous H$_2$O–water vapor

Water is lost during baking in the form of vapor, gaseous H$_2$O, which is always present in the atmosphere. Its relative amount depends on temperature, locality, and altitude. Like other gases, individual H$_2$O molecules are mixed with N$_2$, O$_2$, CO$_2$, CH$_4$, Ar, Ne, He, and so on, in the atmosphere. Due to water vapor in the atmosphere, the average temperature on the earth's surface increases by 30K (Wayne 2000), making earth inhabitable.

Isolated water molecules exhibit unique rotations and vibrations. Energies of microwaves affect the rotation states, and their study is called *microwave spectroscopy*. Energies of infrared (IR) affect the rotation-vibration states, and their study is called *infrared spectroscopy*. Water vapor is transparent to visible light, and evaporation of water cannot be seen by the naked eye. The absorption of IR, however, may be used to monitor the amount of water vapor in a baking chamber.

Solid and liquid H_2O

Molecules in liquids and solids are in close contact, and they attract one another. The attractions are called *intermolecular interactions* and are insignificant in gas. The attraction is a fundamental property called the *van der Waals force*. The polar water molecules attract each other more strongly, because they possess a large dipole moment. Furthermore, water molecules form *hydrogen bonding*, which is a very strong link between a bonded hydrogen atom (O—H) and the oxygen (O) atom of other molecules in the form of O—H − − −O. As is seen later, the molecules in ice are all hydrogen bonded to each other, and a large percentage of the molecules in liquid H_2O, or water, are also involved in hydrogen bonding. In the liquid H_2O, the hydrogen bonding partners rapidly interchange.

The properties of water, ice, and water vapor must be considered in baking, freezing, pressure-cooking, and microwave heating. For example, solid, liquid, and gaseous H_2O transform into each other in the phenomenon called *phase transition*. The temperature and pressure for the transition affect the baking process. However, water molecules in bread dough and cake batter intimately interact with baking ingredients, and the conditions for phase transitions are therefore different from those for pure water.

Water has many abnormal properties. The melting point (mp) and boiling point (bp) are abnormally high for water compared with other compounds of similar molecular mass, as is the *critical temperature*, above which H_2O cannot be liquefied. The abnormal properties are due to the polar water molecules and the energy required to break the hydrogen bonds. Thus, melting ice and evaporation of water molecules from solid or liquid require a lot of energy.

The densities of water and ice are also strange. Ice at 273K is 9% less dense than water, while solids of most substances are denser than their liquids. Thus, ice floats on water extending 9% of its volume above water. Water is densest at 277K (4°C). Being less dense at its freezing point, water freezes from the top down, whereas butter and shortening solidify from the bottom up. The hydrogen bonding and polarity also lead water to have peculiarly high surface tension, dielectric constant, and viscosity.

Solid H_2O—ice

The structure of ice

Water molecules in frozen dough are highly organized in that they are strongly hydrogen bonded to foodstuffs and among themselves in a manner similar to their assembly in ice. Intensive studies of pure H_2O solids have revealed many types of solids. In *ice crystals*, the molecules are highly organized, but molecules in *amorphous solids* order in the same manner as those in the liquid. Thus, amorphous solids are also called *glassy water* or *frozen liquid*. To see the intermolecular relationships of water, one must take a close look at the structure of ordinary ice.

At ambient conditions, *hexagonal ice* (Ih) is formed. The hexagonal symmetry is obvious in snow flakes, and its crystal structure is well known (Kamb 1972). Every oxygen atom has four hydrogen bonds around it, two formed by donating its two H atoms, and two by accepting the

H atoms of neighboring molecules. The hydrogen bonds connecting O atoms are shown in Figure 7.3. Although the positions of the H atoms are random or disordered, the scientific community considers that the hydrogen bonds O—H– – – O extend continuously throughout the crystal.

Two rings marked
by O atoms ⬤
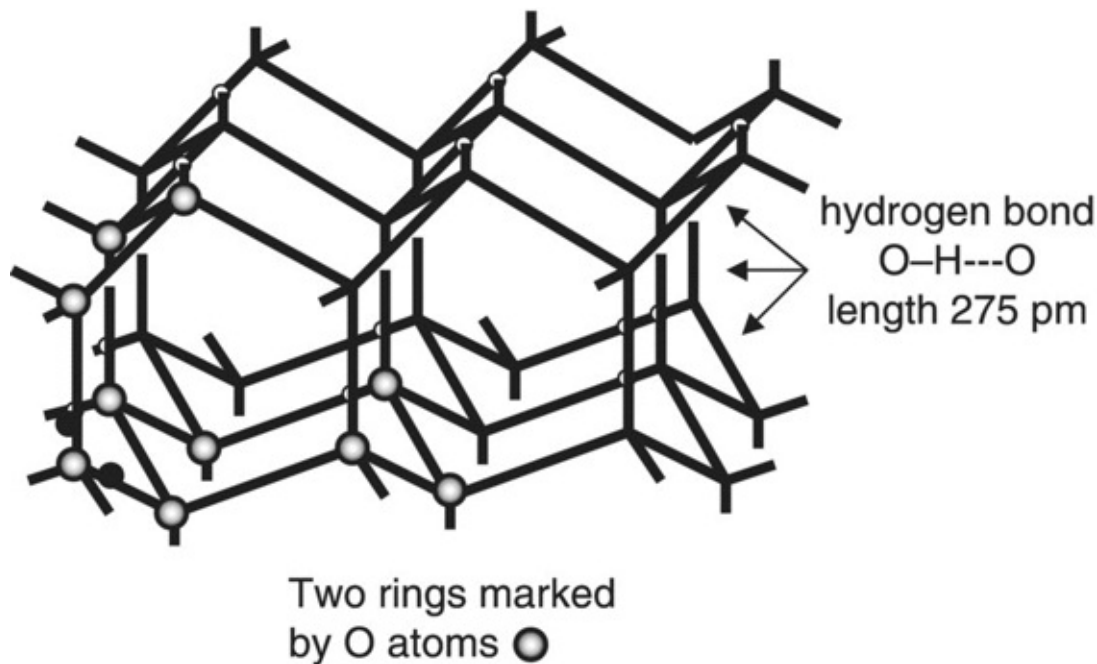
Figure 7.3 The crystal structures of ice, Ih. Oxygen atoms are placed in two rings. Each line represents a hydrogen bond O—H– – –O, and the H atoms are randomly distributed such that on average, every O atom has two O—H bonds of 100pm. The O—H– – –O distance is 275pm. The idealized tetrahedral bond angles around oxygen are 109.5°.

In the structure of Ih, six O atoms form a ring. In Figure 7.3, two-ring configurations are marked by spheres representing the O atoms. Formation of the hydrogen bond in ice lengthens the O—H bond slightly in comparison with those in a single isolated water molecule. All O atoms in Ih are completely hydrogen bonded, except for the molecules at the crystal surface. The natural tendency for water molecules to form the maximum number of hydrogen bonds underlies the formation of solid water phases. Pauling (1960) pointed out that the formation of these hydrogen bonds is partly an electrostatic attraction.

Since only four hydrogen bonds are around each O atom, the structure of Ih has rather large channels from the atomic viewpoint. Under pressure, many other types of ices with their own unique structures are formed. In liquid water, the many tetrahedral hydrogen bonds are formed with immediate neighbors. Water molecules constantly exchange hydrogen-bonding partners, and in so doing the average nearest neighbors usually number more than four. Therefore, water is denser than ice. Hydrogen bonding also takes place when water interacts with other molecules such as proteins and starches containing —NH_2 or —OH groups, which can donate the H atoms or accept them for hydrogen bonding.

Structures of H_2O solids illustrate not only the intermolecular interactions among water molecules, but also interactions of water molecules with bakery ingredients containing >C=O, —OH, >NH, and —NH_2, present in sugar, carbohydrates, proteins, and alkaloids.

Vapor pressure of ice and freeze-drying

Loss of water in frozen food leads to freezer burn, and frozen food can be dried when

desirable. The constant vapor pressure of ice in a closed system at temperature T is called the *equilibrium vapor pressure*, which varies with T. The amount of ice in this equilibrium and the volume enclosing the ice and vapor are immaterial. The detailed data can be found in handbooks; for example, the *CRC Handbook of Chemistry and Physics* (Lide 2003). More recent values between 193 and 273K can also be found in *Physics of Ice* (Petrenko et al. 1999). Ice sublimes at any temperature if the surrounding (partial) vapor pressure is less than the equilibrium pressure. When the vapor pressure is high, molecules deposit onto ice to reduce the vapor pressure.

Equilibrium vapor pressure is a measure of the ability or potential of the water molecules to escape from ice to form a gas. This potential increases as the temperature increases. Thus, the equilibrium vapor pressures of ice, water, and solutions are important quantities. The equilibrium vapor pressure of ice plotted against temperature (T in K) is shown in Figure 7.4. The line indicates equilibrium conditions, and it separates the *P-T* graph into two domains; vapor tends to deposit on ice in one, and ice sublimes in the other. This is the ice-vapor portion of the *phase diagram of water* to be described later in this chapter.
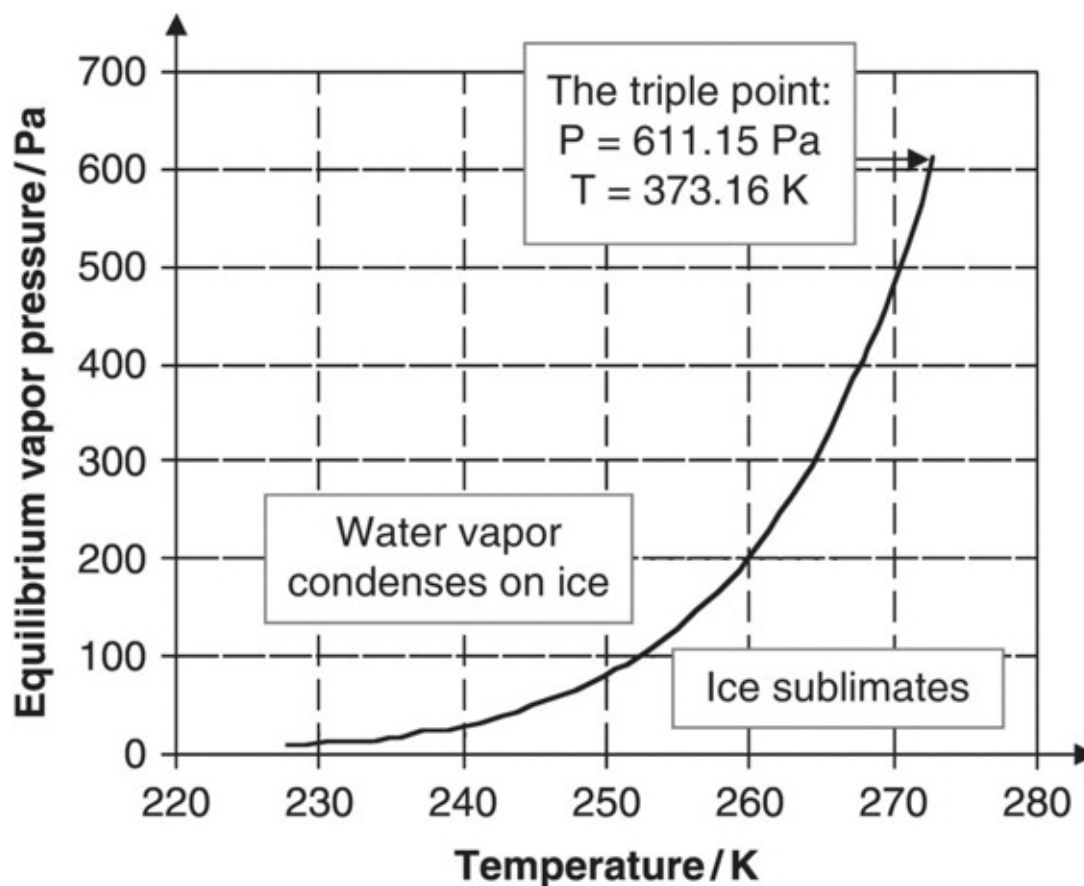
Figure 7.4 Equilibrium vapor pressure (in Pa) of ice as a function of temperature (K).

Liquid H₂O—water

Properties of liquid H₂O

In baking a certain amount of liquid H_2O is added to dissolve, mix, disperse, and wet ingredients. Water also provides a medium for chemical reactions and facilitates heat transfer throughout the volume of the pieces being baked. In the end, some water is left in the finished bakery product. The unique physical and chemical properties of H_2O are closely tied

to its role in baking.

Water has a large *heat capacity* (4.2176J/g/ Kg^{-1}K^{-1} at 273.15K), requiring a lot of heat to raise its temperature. Its heat capacity varies little between 273.15 and 373.15K, but it decreases slightly, reaching a minimum at about 308K, and then rises to 4.2159Jg^{-1}K^{-1} at 373.15K (see Fig. 7.5). Since the variation is small, the temperature rises steadily during the baking process.
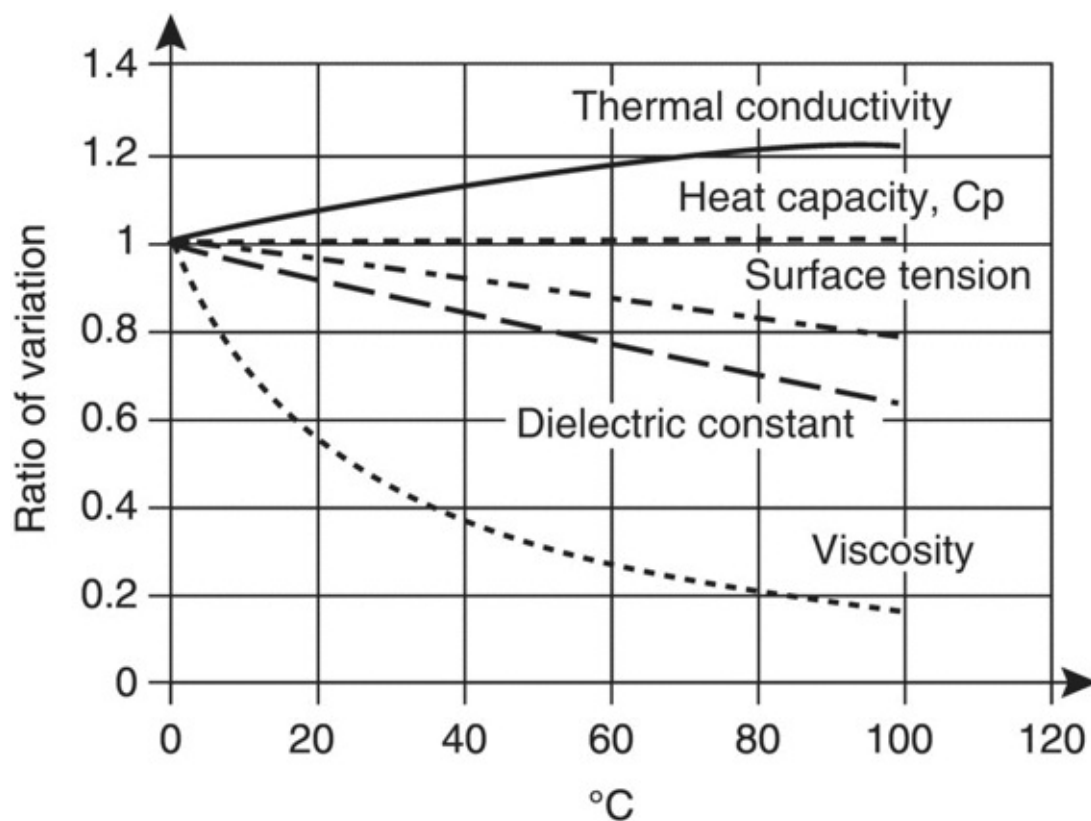
Figure 7.5 Variation of viscosity (1.793mPas), dielectric constant (87.90), surface tension (75.64 mN mT^1), heat capacity Cp (4.2176Jg^{-1}K^{-1}), and thermal conductivity (561.0WK^{-1}, m^{-1}) of water from their values at 273.16K to 373.16K (0 and 100). Values at 273.15K are given.

As mentioned earlier, other properties of water are abnormal as well. The viscosity, surface tension, and dielectric constant of liquid H_2O decrease as temperature increases, see Figure 7.5. These three properties are related to the extent of hydrogen bonding and the ordering of the dipole moments. As thermal disorder increases with rising temperature, these properties decrease. In order to show the variation, the properties at other temperatures are divided by the same property at 273K. The ratios are then plotted as a function of *T*. At 273.15K, all the ratios are unity (1). The thermal conductivity, on the other hand, increases with temperature. Thus, the thermal conductivity at 373K (679.1WK^{-1}m^{-1}) is 1.21 times that at 273K (561.0WK^{-1}m^{-1}). Faster moving molecules transport energy faster. Warm water better conducts heat. Thus, the temperature at the center of a baked piece rises more rapidly when the piece is hot than when the piece is cold.

Densities of other substances are often determined relative to that of water. Therefore the density of water is a primary reference. The variation of density with temperature is well known, and accurate values are carefully measured and evaluated, especially between 273 and 313K (0–40°C). Two factors affect water density. Thermal expansion reduces its density, but the reduced number of hydrogen bonds increases its density. The combined effects resulted

in the highest density at approximately 277K (4°C). Tanaka et al. (2001) has developed a formula to calculate the density within this temperature range, and the *CRC Handbook of Chemistry and Physics* (Lide 2003) has a table listing these values. The variation of water density between the freezing point and the boiling point is shown in Figure 7.6.
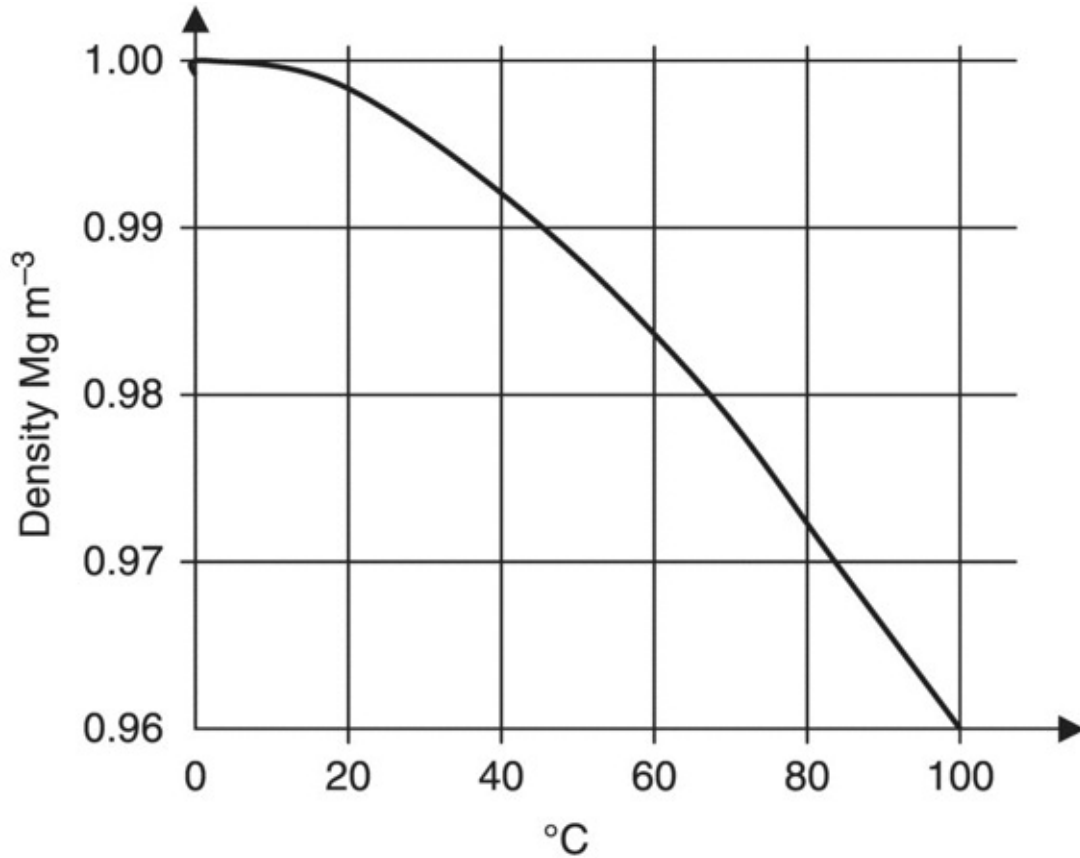
Figure 7.6 The variation of water density as a function of temperature.

Most dry organic baking ingredients are less dense than water, but water wets and penetrates them to provide a good mixture.

Vapor pressure of liquid H_2O

Like ice, the equilibrium vapor pressure of water increases with temperature (Fig. 7.7). At the *triple point*, the vapor pressures of ice and water are the same, 0.611 kPa, and the *boiling point* (373.15K, 100°C) is the temperature at which the vapor pressure is 101.325 kPa (1atm) (see Fig. 7.8). At slightly below 394K (121°C), the vapor pressure is 202.65 kPa (2.00atm). At 473 and 574K, the vapor pressures are 1553.6 and 8583.8 kPa, respectively. The vapor pressure rises rapidly as temperature increases.
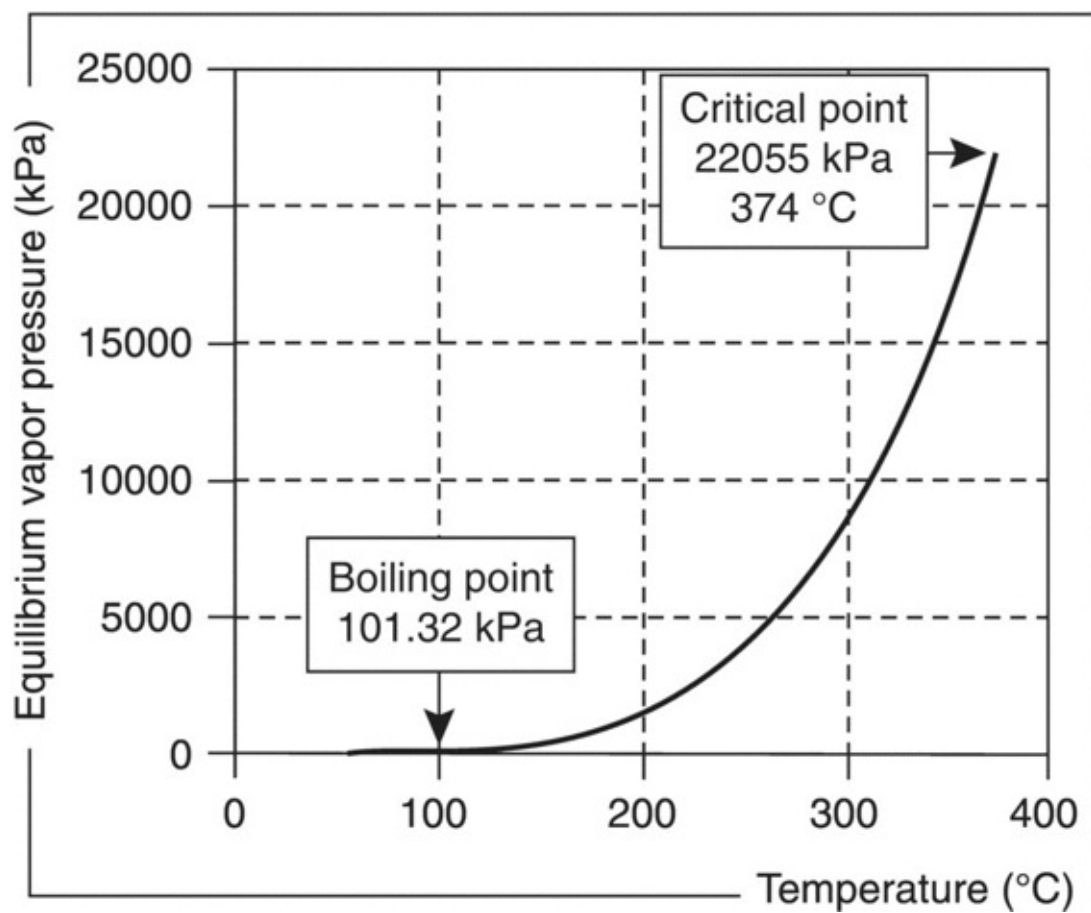
Figure 7.7 Equilibrium vapor pressure of water as a function of temperature.
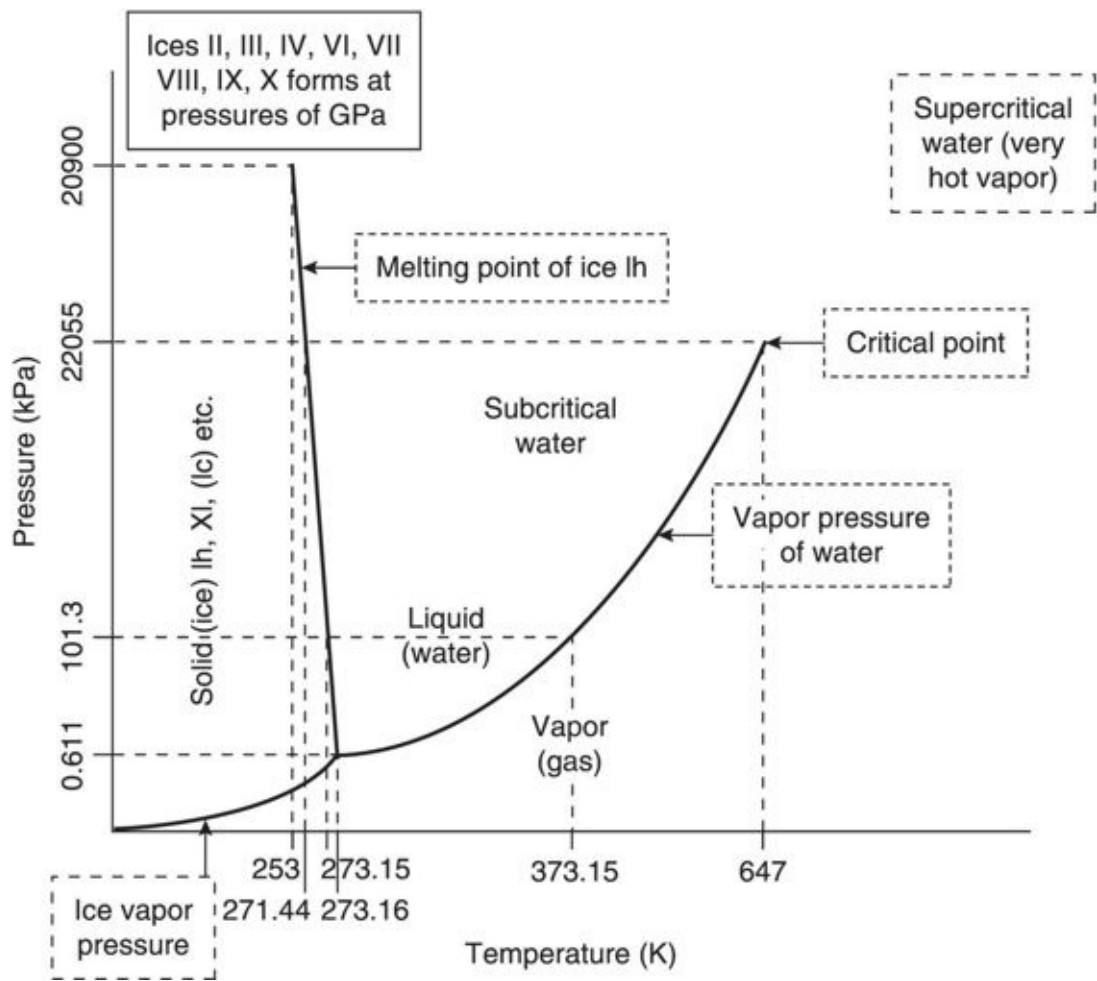
Figure 7.8 A sketch outlining the phase diagram of ice, water, and vapor.

The lowest pressure to liquefy water vapor just below the *critical temperature*, 373.98°C, is 22,055 kPa (217.67atm), and this is known as the *critical pressure*. Above 373.9°C, water vapor cannot be liquefied, and the fluid is called *supercritical water* (see Fig. 7.8).

The partial pressure of H_2O in the air at any temperature is the *absolute humidity*. When the partial pressure of water vapor in the air is the equilibrium vapor pressure of water at the same temperature, the *relative humidity* is 100%, and the air is saturated with water vapor. The partial vapor pressure in the air divided by the equilibrium vapor pressure of water at the temperature of the air is the *relative humidity*, expressed as a percentage. The temperature at which the vapor pressure in the air becomes saturated is the *dew point*, at which dew begins to form. Of course when the dew point is below 273K (0°C), ice crystals (frost) begin to form.

As temperature rises during baking, water becomes vapor in trapped air pockets in the bread dough and cake batter. Rising temperature expands the bubbles, enlarging the gas pockets, unless the gas leaks out. Formation of vapor affects loaf volume and causes sponginess in the bakery product.

Transformation of solid, liquid, and vapor

The dough or batter is a mixture, and it contains fluids and solids. Waters in dough are not pure. Thus, equilibrium conditions for frozen products and for the evaporation of water during the baking process are very different from those of pure water. Yet, phase transitions of water provide an approximate guide for the transformation of water during the baking process.

At 273.16K, ice, liquid H_2O, and H_2O vapor at 611.15Pa coexist and are at equilibrium; the temperature and pressure define the *triple-point* of water. At the normal pressure of 101.3 kPa (1atm), ice melts at 273.15K.

Under ambient pressure, ice often does not begin to form until temperatures are colder than 273.15K, and this is known as *supercooling*, especially for pure water. The degree of supercooling depends on volume, purity, disturbances, the presence of dust, the smoothness of the container surface, and other factors. Crystallization starts by *nucleation*, that is, formation of ice-structure-clusters sufficiently large that they begin to grow and become crystals. Once ice begins to form, the temperature will return to the freezing point. At 234K (−39°C), tiny drops of ultrapure water will suddenly freeze, and this is known as *homogeneous nucleation* (Franks 2000). Dust particles and roughness of the surface promote nucleation and help reduce supercooling for ice and frost formation.

Baking with frozen dough involves transformations among solid, liquid, and gaseous H_2O. Therefore, it is important to understand ice-water, ice-vapor, and water-vapor transformations and their equilibria. A map is helpful in order to comprehend these natural phenomena. Such a map, outlining the temperature and pressure for these transformations, is called a *phase diagram* and is outlined in sketch form in Figure 7.8. A sketch must be used because the range of pressures involved is too large for the drawing to be constructed on a linear scale.

The curves representing the equilibrium vapor pressures of ice and water as functions of temperature meet at the *triple point*, shown in Figure 7.8. The other end of the water-vapor pressure curve is the critical point. The melting points of ice are 271.44, 273.15, and 273.16K

at the critical pressure (22,055 kPa), 101.325 kPa, and 0.611 kPa (triple point), respectively. At a pressure of 200,000 kPa, ice melts at 253K. Thus, the line linking all these points represents the melting point of ice at different pressures. This line divides the conditions (pressure and temperature) for the formation of solid and liquid. Thus, the phase diagram is roughly divided into regions of solid, liquid, and vapor.

Aqueous solutions

Water dissolves a wide range of substances, and nearly all waters related to the bakery industry are *aqueous solutions*, however dilute they are. When water mixes with baking ingredients, the portion of water that strongly interacts with other molecules is *bound water*, whereas the other portion is called *free water*. The latter has soluble components such as electrolytes, sugars, pentosanes, and proteins dissolved in it. The solutes modify the properties of the water.

Melting and boiling points of aqueous solutions

Solutions in baking mixtures probably never behave ideally in the scientific sense, but there are no standards or data for all the situations encountered in baking industry or practice. However, the study of ideal solutions revealed some interesting trends that may serve as a guide for master bakers to consider.

Vapor pressures at a given temperature of most solutions are lower than that of pure water, except the few cases in which the solutes increase the potential for water molecules to escape from the solid or liquid. Vapor pressure affects the melting point, the boiling point, and the osmotic pressure because they are closely related to the vapor pressure.

In general, the vapor pressure of a solution at the normal boiling point is lower than that of pure water, and a higher temperature is required for the vapor pressure to reach 101.3 kPa (1atm). The net increase in the boiling temperature of a solution above that of pure water is known as the *boiling point elevation*.

Ice formed from a dilute solution usually does not contain the solute. Thus, the vapor pressure of ice at various temperatures does not change, but the vapor pressure of a solution is lower than that of ice at the freezing point. Further cooling is required for ice to form due to the lowering of vapor pressure. This difference in temperature is called the *freezing point depression*.

In freezing and boiling a solution of a nonvolatile solute, the solid and vapor contain only H_2O, leaving the solute in the solution. Thus, boiling points of solutions are higher and freezing points are lower. The more concentrated the solutions are, the more the difference. Please note that freezing points and boiling points apply to systems that are at equilibrium. They are different from superheating and super-cooling, which are nonequilibrium phenomena.

A solution containing volatile solutes, for example, alcohol in water, will have a total vapor pressure due to all volatile components in the solution. Its boiling point is no longer that of water alone. Freezing point depression and boiling point elevation are both related to the vapor pressure. In bakery products, both volatile and nonvolatile substances are present. The gas released contains water and volatile substances either present as ingredients at the start of baking or produced during heating. The vapors produced in baking processes are very complicated because fluids in dough and batter deviate from ideal solutions.

Osmotic pressure of aqueous solutions and reverse osmosis

Osmotic pressure is the pressure that must be applied to the side of the solution to prevent the flow of pure water passing a semipermeable membrane into the solution. In other words, water molecules have a tendency to move from dilute to concentrated solutions. Osmotic pressure is a driving force for water to diffuse into grains and starch granules. Therefore, time is required for dough to develop after the flour and water are mixed. Of course, polarity, hydrogen bonding, capillary action, and other factors also affect the interaction of water with other baking ingredients.

Applying pressure to concentrated solutions reverses the direction of water diffusion due to osmotic pressure. This is the principle for *water treatment by reverse osmosis*, which is often used in areas where seawater is available, but not freshwater. Water so treated may contain few of the minerals required for yeast, and yeast foods containing supplementary minerals may be required to rectify the situation in order to produce good quality bread.

Solution of electrolytes

Charged ions in solutions move when driven by an electric potential, and these solutions conduct electricity. Therefore, ion-containing substances such as acids, bases, table salts, baking soda, baking powder, and cream of tartar are *electrolytes*. The high dielectric constant of water reduces the attractions of ions within ionic solids; thus water dissolves them. Furthermore, the polar water molecules surround ions, forming *hydrated ions*. The concentration of all ions and molecular substances in a solution contributes to the osmotic pressure mentioned in the previous section.

Water can also be an acid or a base, because H_2O molecules can receive or provide a proton (H^+). Such an exchange by water molecules in pure water, forming *hydrated protons*, (H_3O^+ or $(H_2O)_4H^+$), is *self-ionization*. However, as will be shown below, the extent of self-ionization is small, and pure water is a very poor conductor.

Self-ionization of water

Acidity of dough and batter is due to the presence of acids, bases, or salts in the ingredients, but the self-ionization of water also plays an important role. Often, the pH is a quantity used to describe the acidity, and its meaning will be explained.

The self-ionization of water is a dynamic equilibrium,

$$H_2O(l) \leftrightarrow H^+(aq) + OH^-(aq), K_w = [H^+][OH^-]$$
$$= 10^{-14} \text{ at } 298 \text{ K and } 1 \text{ atm}$$
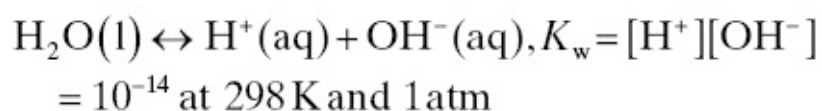
where $[H^+]$ and $[OH^-]$ represent the *molar concentrations* (in mol L^{-1}) of H^+ (or H_3O^+) and OH^- ions, respectively, and K_w is the *ion product of water*. Values of K_w under various conditions have been evaluated theoretically (Marshall and Franck 1981, Tawa and Pratt 1995). Solutions in which $[H^+]=[OH^-]$ are said to be *neutral*. Both *pH* and *pOH*, as defined by the following equations, have a value of 7 at 298K for a neutral solution:

$$pH = -\log_{10}\left[H^+\right] = pOH = -\log_{10}[OH^-] = 7$$
$$\text{(at 298 K)}$$

H^+ represents a hydrated proton (H_3O^+), which dynamically exchanges a proton with other water molecules. The self-ionization and equilibrium are present in water and all aqueous solutions. Note that pH and pOH are exponents of their respective ion concentrations: an increase of 1.0 for the pH indicates a tenfold decrease of $[H^+]$.

Solutions of acids and bases

Acidity and acid-base reactions play important roles in baking. Acidity affects the activity of yeast, and acid-base reactions are involved in chemically leavened bakery products. Both cases produce carbon dioxide, CO_2, which dissolves in water, forming a solution with complicated equilibria. The acidity of phosphoric acid, baking soda, and cream of tartar are also complex. Some quantitative consideration will contribute to appreciation of the effects of acids and bases in baking science.

Strong acids $HClO_4$, $HClO_3$, HCl, HNO_3, and H_2SO_4 completely ionize in their solutions to give H^+ (H_3O^+) ions and anions: ClO_4^-, ClO_3^-, Cl^-, NO_3^-, and HSO_4^-, respectively. *Strong bases* $NaOH$, KOH, and $Ca(OH)_2$ also completely ionize to give OH^- ions and Na^+, K^+, and Ca^{2+} ions, respectively. In an acidic solution, $[H^+]$ is greater than $[OH^-]$. For example, in a $1.00\,molL^{-1}$ HCl solution at 298K, $[H^+]=1.00\,mol/L$, pH=0.00, and $[OH^-]=10^{-14}mol/L$.

Weak acids such as formic acid ($HCOOH$), acetic acid (HCH_3COO), ascorbic acid ($H_2C_6H_5O_6$), oxalic acid ($H_2C_2O_4$), carbonic acid (H_2CO_3), benzoic acid (HC_6H_5COO), malic acid ($H_2C_4H_4O_5$), lactic acid ($HCH_3CH(OH)COO$), and phosphoric acid (H_3PO_4) also ionize in their aqueous solutions, but not completely. The ionization of acetic acid, is represented by the equilibrium

$$HCH_3COO(aq) \leftrightarrow H^+(aq) + CH_3COO^-(aq),$$
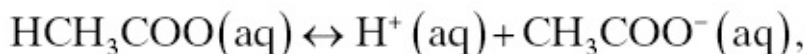
$$K_a = \frac{\left[H^+\right]\left[CH_3COO^-\right]}{\left[HCH_3COO\right]} = 1.75 \times 10^{-5} \text{ at } 298\,K$$

where K_a, as defined above, is the *acid dissociation constant*. In the expression, $[H^+]$, $[CH_3COO^-]$, and $[HCH_3COO]$ represent *equilibrium molar concentrations* of the species in square brackets.

The solubility of CO_2 in water increases with partial pressure of CO_2, according to Henry's law. The chemical equilibrium for the dissolution is

$$H_2O(l) + CO_2(g) \leftrightarrow H_2CO_3(aq)$$
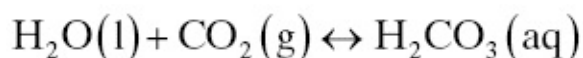
Of course, H_2CO_3 dynamically exchanges H^+ and H_2O with other water molecules, and this weak *diprotic acid* (two-proton acid) ionizes in two stages, with the acid dissociation

constants K_{a1} and K_{a2}.

$$H_2O + CO_2(aq) \leftrightarrow H^+(aq)\, HCO_3^-(aq), K_{a1}$$
$$= 4.30 \times 10^{-7} \text{ (at 298 K)}$$

$$HCO_3^-(aq) \leftrightarrow H^+(aq) + CO_3^{2-}(aq), K_{a2}$$
$$= 5.61 \times 10^{-11}$$
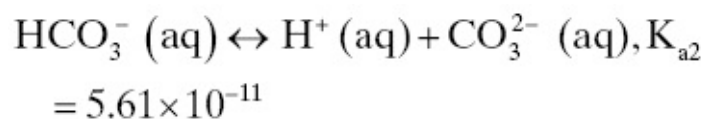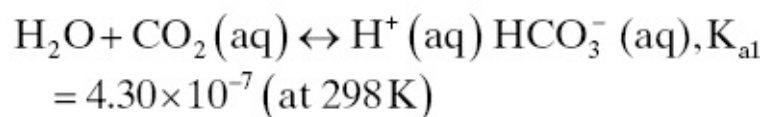
Constants K_{a1} and K_{a2} increase as temperature rises, but the solubility of CO_2 decreases. At 298K, the pH of a solution containing 0.1mol/L H_2CO_3 is 3.7. At this pH, acidophilic organisms survive and grow; however, most pathogenic organisms prefer a neutral environment, and they cease growing. Soft drinks contain other acids—citric, malic, phosphoric, ascorbic acids, and other acids—that lower the pH further.

All three hydrogen ions in phosphoric acid (H_3PO_4) are ionizable, and it is a *triprotic acid* (tree-proton acid). Acids having more than one dissociable H^+ are called *polyprotic acids*.

Ammonia and many nitrogen-containing compounds are *weak bases*. The ionization equilibrium of NH_3 in water and the *base dissociation constant K_b* are

$$NH_3 + H_2O \leftrightarrow NH_4OH \leftrightarrow NH_4^+(aq) + OH^-$$

$$K_b = \frac{[H^+][OH^-]}{[NH_4OH]} = 1.70 \times 10^{-5} \quad \text{at 298 K.}$$

Other weak bases react with H_2O and ionize in a similar way.

The ionization or dissociation constants of inorganic and organic acids and bases are extensive, and they have been tabulated in various books: for example, Perrin (1965, 1982) and Kortum et al. (1965).

Buffer solutions

Waters in moist dough and bakery products are solutions of many substances: weak acids, weak bases, electrolytes, proteins, and so on. These chemicals provide a *buffer action* so that the pH will not change easily. Thus, a quantitative consideration regarding buffer solutions is presented here.

A solution containing a weak acid and its salt, or a weak base and its salt is a *buffer solution*, since its pH changes little when a little acid or little base is added. For example, nicotinic acid ($HC_6H_4NO_2$, niacin, a food component) is a weak acid with $K_a = \log_{10}K_a = 4.76$):

$$HC_6H_4NO_2 = H^+ + C_6H_4NO_2^-, K_a$$
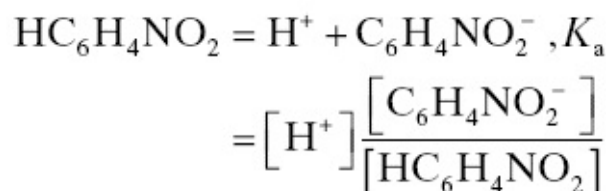
$$= [H^+]\frac{[C_6H_4NO_2^-]}{[HC_6H_4NO_2]}$$

$$pH = pK_a + \log \left\{ \frac{\left[C_6H_4NO_2^- \right]}{\left[HC_6H_4NO_2 \right]} \right\}$$

The last equation is called the Henderson-Hesselbach Equation, and it gives the pH in terms of the *molar ratio* ($[C_6H_4NO_2^-]/[HC_6H_4NO_2]$) of the salt to the acid. In a solution containing niacin and its salt, $[C_6H_4NO_2^-]$ is the concentration of the salt and $[HC_6H_4NO_2]$ is the concentration of niacin. The pair, $HC_6H_4NO_2$ and $C_6H_4NO_2^-$, are called a *conjugate acid* and a *conjugate base*, respectively. So, for a general acid and its conjugate base, the pH can be evaluated using the Henderson-Hessebalch Equation.

$$pH = pK_a + \log \left\{ \frac{[base]}{[acid]} \right\} \quad \begin{array}{l} \text{(Henderson -} \\ \text{Hesselbach Equation)} \end{array}$$

Adding H^+ converts the base into its conjugate acid, and the adding OH^- converts the acid into its conjugate base. Adding an acid or a base changes the [base]/[acid] ratio, causing a small change in the pH if the initial ratio is close to unity. Following this equation, the most effective buffer solution for a desirable pH is obtained by using an acid with pK_a value similar to the desired pH value, and then adjusting the concentration of the salt and the acid to obtain the ratio that gives the desired pH. For example, the pK_a for $H_2PO_4^-$ is 7.21, and mixing KH_2PO_4 and K_2HPO_4 in the appropriate ratio will give a buffer solution with pH7. However, more is involved in the art and science of making and standardizing buffer solutions. For example, the ionic strength (related to the concentration of all ions) must be taken into account.

The phosphoric acid and bicarbonate ions and many other soluble molecules in bakery products play a buffering role in keeping the pH stable. The production of weak acids and bases during the process of mixing, fermentation, and baking causes the pH to change, despite the buffer action. The equilibria of all acids and bases plus that due to the self-ionization of water determine the pH of the solution in bakery materials.

Hard waters and their treatments

Between 40 and 50% (by mass) of bread dough is water. Water hardness affects dough quality, fermentation, and the final products. Natural waters contain minerals and are usually hard, but the hardness varies depending on the source, region, and time. Thus, an overview of hard water and its treatment are necessary for baking science and technology.

Waters containing dissolved CO_2 (H_2CO_3) are acidic due to the equilibria

$$H^+ (aq) + HCO_3^- (aq) \leftrightarrow H_2CO_3 (aq) \leftrightarrow$$
$$H_2O + CO_2 (g)$$

$$HCO_3^- (aq) \leftrightarrow H^+ (aq) + CO_3^{2-} (aq)$$
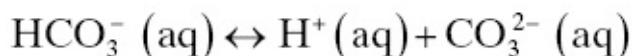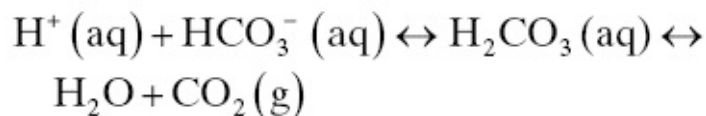
Why the solution is acidic was explained in the previous section. Acidic waters dissolve

$CaCO_3$ and $MgCO_3$, and waters containing Ca^{2+}, Mg^{2+}, HCO_3^-, and CO_3^{2-} ions are *temporary hard waters* as the hardness is removable by boiling, which reduces the solubility of CO_2. When CO_2 is driven off, the solution becomes less acidic due to the above equilibria. Furthermore, reducing the acidity increases the concentration of CO_3^{2-}, and the solids $CaCO_3$ and $MgCO_3$ precipitate.

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$

$$Mg^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MgCO_3(s)$$
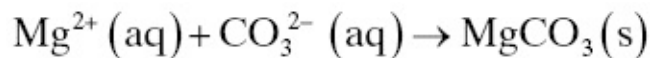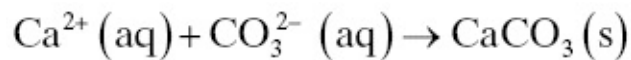
Solid (s) $CaCO_3$ and $MgCO_3$ form scales in boilers, pipes, kettles, and coffee machines.

For water softening by *lime treatment*, the amount of dissolved Ca^{2+} and Mg^{2+} is determined first; then an equal number of moles of lime, $Ca(OH)_2$, is added to remove them by the following reactions:

$$Mg^{2+} + Ca(OH)_2(s) \rightarrow Mg(OH)_2(s) + Ca^{2+}$$

$$Ca^{2+} + 2HCO_3^- + Ca(OH)_2(s) \rightarrow 2CaCO_3(s) + 2H_2O$$
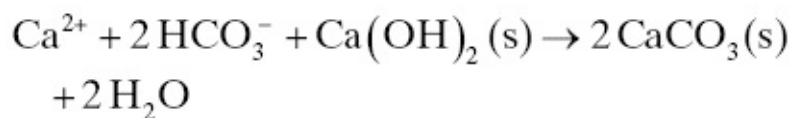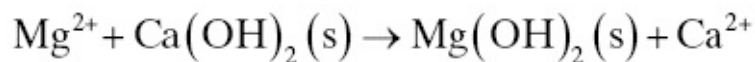
Permanent hard waters contain sulfate (SO_4^{2-}), Ca^{2+}, and Mg^{2+} ions. Calcium ions in the sulfate solution can be removed by adding sodium carbonate due to the reaction

$$Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3(s) + 2Na^{2+}$$
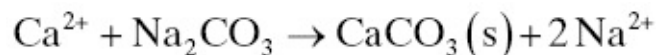
Hard waters cause scales or deposits to build up in boilers, pipes, and baking equipment. *Ion exchange* using resins or zeolites is commonly used to soften hard waters. The calcium and magnesium ions are taken up by the resin or zeolite, replacing them with sodium or hydrogen ions. Alternatively, a pressure is applied to the hard water to force water molecules, but not ions, through semipermeable membranes. This *reverse osmosis* technique makes use of the osmotic pressure described earlier.

However, water softening replaces desirable calcium, magnesium, and other ions with sodium ions. Thus, soft waters are not suitable for drinking or breadmaking. Water containing less than 50mg/L of these substances is considered soft; 50–150mg/L moderately hard; 150–300mg/L hard; and more than 300mg/L very hard. Moderately hard water containing 50–100mg/L (50–100ppm calcium carbonate) is favored for breadmaking, since soft waters yield soft sticky dough (Pyler 1988). Water hardness can be determined by titration, and many kinds of commercial testing kits are available from water conditioning companies.

Ions in baking science

Ions affect yeast activity during fermentation, and they also affect the quality of bakery products, because they interact with proteins of wheat flour. These have been covered in the

chapter on water and in other chapters of *Baking Science and Technology* (Pyler 1988). The study of effects of ions on bread-making continues (Vadlamani and Seib 1999). For the production of yeast, NH_4^+ Ca^{2+}, Mg^{2+}, Fe^{2+}, Zn^{2+}, and anions of sulfate and phosphate with different charges are also added as *yeast food* in addition to other yeast nutrients. Furthermore, calcium-protein interaction strengthens the gluten for gas retention, leading to even crumb in bread. On the other hand, very hard water retards fermentation, because calcium ions strengthen the gluten structure too much.

As mentioned earlier, minerals or salts are completely ionized when dissolved in water. For example, calcium ions from $CaCl_2$ are indistinguishable from $CaCO_3$. When both salts are dissolved, the solution contains Ca^{2+}, Cl^-, HCO_3^{2-}, and CO_3^{2-} due to the equilibria discussed earlier. Similarly, the OH^- ions from NaOH, $Mg(OH)_2$, and $Ca(OH)_2$ are indistinguishable and are mixed in the solution. An increase of OH^- ions increases the pH, but an increase of CO_3^{2-} also increases the pH due to the equilibrium

$$CO_3^{2-}(aq) + H_2O \leftrightarrow HCO_3^-(aq) + OH^-(aq)$$

The H^+ and OH^- ions, or acidity, affect the activities of yeast more than other ions.

Ammonium ions, NH_4^+, are also known to enhance yeast activity (Pyler 1988), but the concentration of these ions is related to pH due to the equilibrium

$$NH_4^+(aq) + H_2O \leftrightarrow NH_3(aq) + H_3O^+$$
$$(aq, \text{same as } H^+)$$
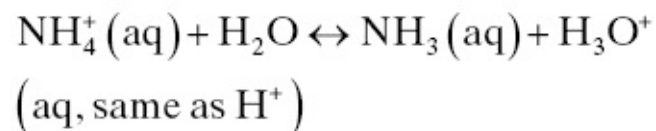
Yeast is most active between pH4 and 5. However, due to the complexity of the ingredients, the effect of a specific ion is hard to isolate and study, because one cannot simply add one type of ion. Every positive ion must be accompanied by a negative ion, and vice versa.

Hydrophilic and hydrophobic effects in baking

At the beginning of the chapter, hydrophilic and hydrophobic baking ingredients were discussed. A closer look at the role of water in the art and science of baking is now in order.

The *hydrophilic effect* refers to the hydrogen bonding, polar-ionic, and polar-polar interactions with water molecules, which lower the energy of the system and make ionic and polar substances soluble. The lack of strong interactions between water molecules and the *lipophilic* or nonpolar molecules that causes hydrophobic molecules to stay together in the presence of water is called the *hydrophobic effect*, a term coined by Charles Tanford (1980). The hydrophobic effect also applies to the non-polar portions of amphiphilic molecules. These effects are present in the baking processes, because hydrophilic, lipophilic, and amphiphilic ingredients are mixed and heated.

Hydrophilic and hydrophobic baking ingredients bind to each other by amphiphilic *emulsifiers* that contain both hydrophilic and hydrophobic parts. In liquid systems, they form colloids or suspensions such as oil in water (milk and dairy cream) and water in oil (butter and shortening). Emulsifiers are also called *surfactants* or *wetting agents* (e.g., in soaps and detergents). Egg white and milk have been used to enrich proteins in bakery products, but they also contain emulsifiers. Emulsifiers are used to aid in aeration (foaming), dispersion, lubrication, mixing, water absorption, gas retention, and agglomeration of baking ingredients. They also modify viscosity, condition the dough, increase loaf volume, and inhibit crystallization (retrogradation) of starch in bread. Therefore, food emulsifiers are vital ingredients in baking.

Milk, butter, and egg enhance dough quality with their proteins and *lecithins*, which are emulsifiers that may be viewed as a derivative of triglycerides, in that one of the fatty acids is replaced by phosphor-choline (as shown in Figure 7.9).

$$H_2C-O-C(=\mathbf{O})-R \quad (R = CH_{2n+1})$$
$$H-\overset{|}{C}-O-C(=\mathbf{O})-R' \quad (R' = CH_{2n})$$
$$H_2\overset{|}{C}-O-P(=\mathbf{O})-O-CH_2-CH_2-\mathbf{N^+}(CH_3) \text{ (phosphocholine)}$$
$$\overset{|}{O^-}$$
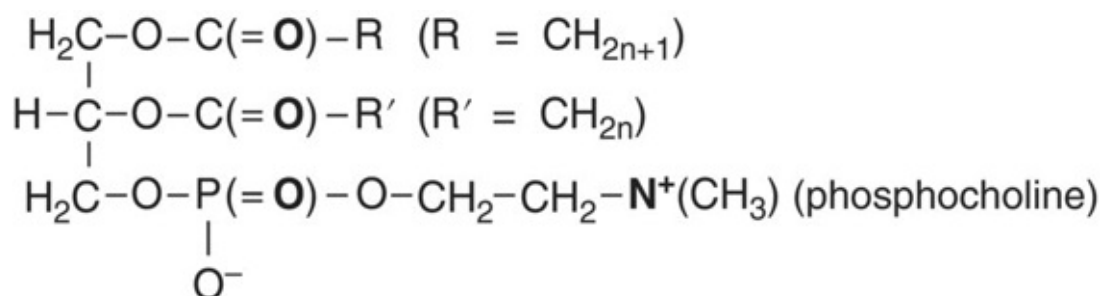
Figure 7.9 Sketch of lecithin structure.

In the structure shown in Figure 7.9, R and R' represent a saturated or unsaturated hydrocarbon (C and H) chain of the fatty acid. These chains are hydrophobic. The three hydrophilic groups are O, OH, and N^+ (shown in bold). The emulsifier shown here produces fatty acids, phosphate, and basic choline when completely hydrolyzed. *Cephalins* are closely related to lecithin, but ethanolamine, $HOCH_2CH_2 NH_2$, replaces the choline, $HOCH_2CH_2N^+(CH_3)_3$, in the structure shown above.

By the same token, di- and monoglycerides have one and two hydrophilic groups (OH), respectively. For example, glycerol monostearate is a fatty solid that is a commonly used emulsifier. These and their derivatives containing hydrophilic groups are also emulsifiers.

They are present naturally in plants and animals, so that fats and oils intimately tie to natural hydrophilic materials in living organisms. For example, egg yolk and soybean have plenty of lecithins and cephalins. Emulsifiers keep the suspensions stable, and they incorporate air bubbles in cake batters and creams.

Emulsifiers with free carboxylic groups have the ability to bind gluten. Some emulsifiers such as diacetyl tartaric acid esters of monoglycerides and sodium stearoyl lactylates strengthen gluten to retain carbon dioxide produced during fermentation or chemical reaction. They enhance the ability of the dough to retain gases, improving the loaf volume of bread.

Catalyzed by enzymes and bases, lipids such as triglycerides react with water to produce di- and monoglycerides and fatty acids during the baking process. Thus, emulsifiers may be produced in mixing, fermentation, baking, and storage.

Gelatinization of starch

Water and starch are two basic baking ingredients needed in almost all bakery products. In the presence of water, starch granules swell and gelatinize when heated. The polar water molecules seek hydrophilic molecules or ions, especially those having the ability to form hydrogen bonds. Starch consists of such molecules, whose own characteristics are inviting to water molecules.

From a chemical viewpoint, starches are polymers of six-carbon sugars called *polysaccharides*. Figure 7.10 shows the 1,4 linkage of three six-carbon sugars in amylose, the possible sites for hydrogen bonding, and the ring-shaped glucose units. Three types of oxygen atoms are present: OH groups, ring O, and 1,4-linking O. The three OH groups per sugar unit are possible sites for hydrogen bonding among themselves or with water molecules. Polymers containing only linear chains are *amylose*, whereas polymers containing additional 1,6-linked branches are *amylopectin*.
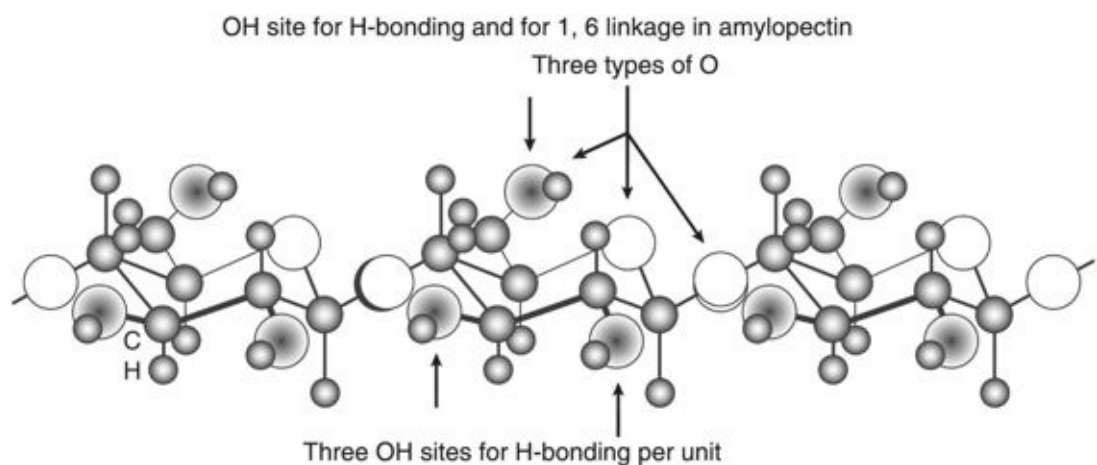
Figure 7.10 The 1,4 linkage of three six-carbon glucose units in the formation of amylose.

Cereal grains consist of starch granules (French 1984). Each granule has a small quantity of granule-associated proteins that might be responsible for the synthesis of polysaccharides, because most of them are granule-associated starch synthase (Han and Hamaker 2001). As the molecules grow and mature, they pack tightly due to inter- and intrachain hydrogen bonds. The granules consist of layers of crystalline and amorphous zones after drying. However, some water molecules remain, bridging the chains with hydrogen bonds. It is not surprising that dry flours contain between 10 and 15% moisture depending on the source (Pyler 1988).

Water slowly seeps into the granules forming hydrogen bonds to the chains due to capillary action, osmotic pressure, diffusion, and polar-polar attraction. Therefore, the granules slowly swell when surrounded by water. Increasing the temperature accelerates water infiltration into the granules. At high temperatures, starch molecules leak out of the granule and gelatinize. Due to limited amount of water in bread baking, starch granules deform, forming an amorphous mass.

The long polysaccharide molecules suspend in water randomly and form hydrogen bonds with water molecules. This affects other water molecules not directly hydrogen bonded to the polymer. The viscosity of the starch-water mixture increases as a result, and a paste is formed

when starch molecules are close to one another. In some crispy cookies, gelatinization may not occur due to lack of water. In these recipes, lipids, proteins, and caramel hold all the ingredients together.

The amylose in the paste or gel has a tendency to crystallize, known as *retrogradation*, which is responsible for bread staling. Certain emulsifiers form complexes with amylose to retard retrogradation. For example, monoglycerides of saturated straight-chain fatty acids are particularly effective for retarding retrogradation. Their presence in bread prolongs shelf life. Crystallized amylose molecules in staled bread are randomized during reheating, but of course, bread staling also involves complicated irreversible changes, such as loss of moisture and flavor.

When amylose and amylopectin leak out, the granule-associated proteins form granule ghosts (Han and Hamaker 2001, Li et al. 2003). These proteins may also be water barriers preventing the granule from swelling at low temperatures, but their structure and function are not certain yet.

Catalyzed by enzymes, starch molecules react with water, breaking down into disaccharides and monosaccharides that are sweet, and they further react with free amino acids to produce a very large number of volatile compounds. Various chemical reactions take place when the dough is being mixed, fermented, and baked. Baltes and Song (1994) chemically analyzed the aroma compounds in wheat bread, and they estimated that 375 aroma compounds had been identified. Nonenzymatic or Maillard browning reactions during heating produces many flavoring compounds.

Water and proteins

Flours contain various amounts of proteins, polymers of thousands of amino acids belonging to 20 different but common amino acids. Water and proteins provide an elastic mass for the dough that retains leavening gas to achieve the spongy crumb of bread. The biosynthesis and biochemistry of protein are very complicated (Kuktaite 2004), but their formations and structures are based on some simple principles. Their abilities to intimately interact with water molecules give them desirable features for baking industries.

An amino acid has an amino group NH_2 and an acid group COOH attached to a carbon atom, which is bonded to a H and another group R. The difference in R gives rise to the 20 different amino acids.

The amino and acid groups of two amino acids react to form a *peptide bond*. The formation and hydrolysis of the peptide bond involves water in the reaction illustrated in Figure 7.11.
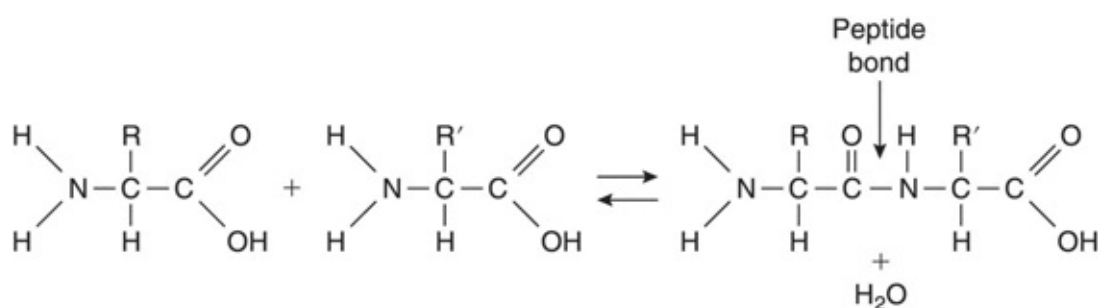
Figure 7.11 Water in the formation and hydrolysis of the peptide bond between two amino acids.

Among the 20 common amino acids, the side chains R of eight are nonpolar, and those of seven are polar, containing —OH, >C=O, or —SH groups. These two side chain types make the hydrophobic and hydrophilic portions of proteins. The Rs in aspartic and glutamic acid contain an additional acid group —COOH, whereas the R in arginine, histidine, and lysine contains basic —NH or —NH$_2$ groups. Therefore, proteins can have both acidic and basic sites to donate and accept protons (H^+). For example, aspartic acid (Asp=(COOH) CH_2C (NH_3^+) (COO^-)) has four forms due to adding or losing protons at different pH values of the solution. It behaves as a triprotic acid, as indicated by the equilibria (the aspartic acid carrying no net charge, is represented by Asp)

$$AspH^+ \leftrightarrow Asp + H^+$$

$$Asp \leftrightarrow Asp^- + H^+$$

$$Asp^- \leftrightarrow Asp^{2-} + H^+$$
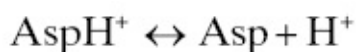
When incorporated in the protein, aspartic acid behaves as a diprotic acid, losing one ionizable H^+, due to the peptide bonding. Therefore, a protein may carry positive, negative, or no net charge depending on the pH of the water medium. The pH of the solution when the

protein carries zero net charge is called the *isoelectric point*, and the solubility of the protein is lowest at this point. Water interacts with proteins and changes their configurations.

Hydrogen bonding, ionic attraction, hydrophilic, and hydrophobic interactions determine the chain configuration, folding, and interchain relationships. In addition to these interactions, there are also the forming and breaking of sulfur-sulfur bridges in various parts of the same chain or in different chains. Oxidation of the amino acid cysteine (CySH) gives cystine (Cys—S —S—Cys), and reducing agents cause the reverse reaction. The S-S bridges (cross-) link the chains into a three-dimensional network. The helical and folded chains provide elasticity, whereas the sliding among chains provides viscosity.

Analysis and classification of proteins are often based on their affinity to water, isoelectric point, or function. Other properties such as molecular weight, chain configuration, interchain relationships, and folding are also important. Depending on the focus, the classification of proteins varies.

Wheat proteins consist of the structural proteins (albumins and globulins), and the storage proteins (gliadins and glutenins). Gluten consists mostly of storage proteins (Pyler 1988). When water is added to flour, the insoluble proteins form an elastic mass called gluten. In breadmaking, gluten provides the structural properties of the dough, and it has the ability to form a film around leavening gas bubbles. The proper type and level of protein is essential for a good gluten mass for quality bread, as is the adequate mixing or kneading of lipids, water, starch, and protein. Molecules of gliadins do not associate with each other, but molecules of glutenins form interchain bridges. Rigorous and excessive mechanical-mixing, however, can break the chains, weakening the protein-protein tangling and leading to sub-standard bread.

Microwave baking

Microwaves have been combined with other heat sources for baking bread and cakes (Keskin et al. 2004). Real dry ingredients do not get warm in microwaves, but microwaves cause water to heat up (Nelson and Datta 2001). Since hot water evaporates, the temperature of the food being baked does not get much above 373K (100°C). Microwave-baked goods lose water, and the foods become very dry when overmicrowaved. Microwave-baked goods seldom get brown, and their flavors cannot match those of oven-baked goods. However, food science researchers are trying to make use of this timesaving technology, and progress is being made. New ingredients are being sought that will react when baked by microwaves to give comparable colors and flavors.

Potatoes are often oven baked, but food processors are switching to baking them with microwaves. Microwave baking of potatoes takes only approximately 5 minutes, depending on the size and variety potato. Starch close to the surface gelatinizes first, and gelatinization migrates inward. A little longer is required for the whole potato to reach a desirable texture for enjoyable eating. Microwave baking is very different from boiling or oven baking of potatoes (Wilson et al. 2002).

Microwave technology is complicated, but one can easily imagine that microwaves of different frequencies have different effects on food (Decareau and Peterson 1986).

Water activity

The water content of dough is critical for both the baking process and the final product. The humidity of the atmosphere around the dough and during the baking process is also important, because it affects water loss. Water provides lubrication when the bakery product is being eaten, affecting its texture. Therefore, water evaporation from and condensation on food is an important concern.

Intermolecular attractions between water and food molecules mutually change their properties. Waters in food are not pure. They are solutions or a component in a mixture in which the molecules strongly interact with one another. Water molecules in vapor, liquid, and solid phases react and interchange with those in solutions and in food. The tendency to react and interchange with each other is called the *chemical potential*, μ. At equilibrium, the potential of water in all phases and forms must be equal at a given temperature, *T*. The potential, μ, of the gas phase is defined by the expression

$$\mu = \mu_w + RT \ln\left(\frac{p}{p_w}\right),$$

where μ_w is the potential of pure water, R is the gas constant (8.3145 Jmol^{-1} K^{-1}), *p* is the partial water vapor pressure, and p_w is the vapor pressure of pure water at temperature *T*. The ratio p/p_w is the *water activity* a_w (= p/p_w), although it is also called *relative vapor pressure* (Fennema and Tannenbaum 1996). The difference between these two terms is small, and for simplicity a_w, as defined, is widely used in food science. For ideal solutions and for most moist foods, a_w is less than unity ($a_w < 1.0$) (Troller 1978).

Both water activity and relative humidity are fractions of the pure-water vapor pressure. Water activity can be measured in the same way as humidity. Water activity and water content have a sigmoidal relationship (Fig. 7.12). As water content increases, so does a_w: $a_w = 1.0$ for infinitely dilute solutions, $a_w > 0.7$ for dilute solutions and moist foods, and $a_w < 0.6$ for dry foods. Of course, the precise relationship depends on the food. In general, if the water vapor of the atmosphere surrounding the food is greater than the water activity of the food, water is adsorbed; otherwise, desorption takes place. The water activity reflects the combined effects of water-solute, water-surface, capillary, hydrophilic, and hydrophobic interactions.
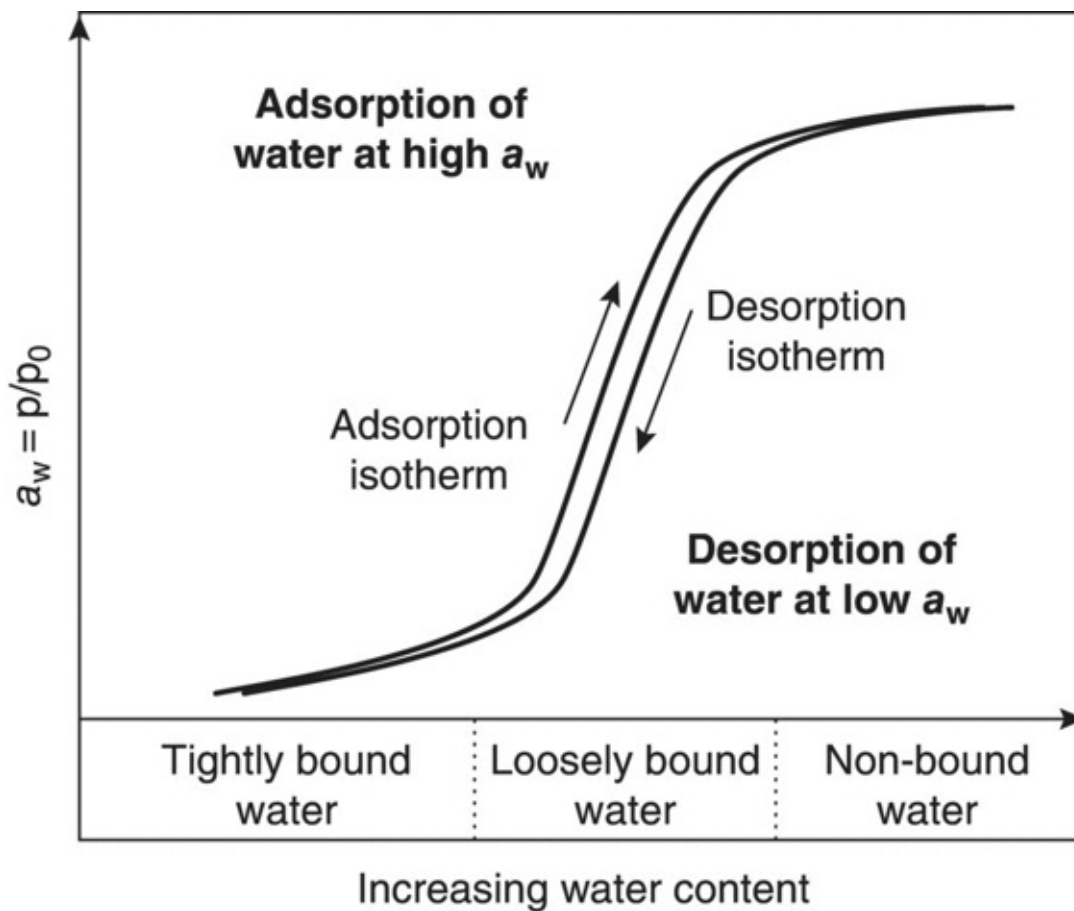
Figure 7.12 Nonequilibrium or hysteresis in desorption and adsorption of water by foodstuff. Arbitrary scales are used to illustrate the concept for a generic pattern.

The water activity is a vital parameter for food monitoring. A plot of a_w versus water content is called an *isotherm*. However, desorption and adsorption isotherms are different ([Fig. 7.12](#)), because this is a nonequilibrium system. Note that isotherms in most other literature plot water content against a_w, the reverse of the axes of [Figure 7.12](#), which is intended to show that a_w is a function of water content.

Water in food may be divided into tightly bound, loosely bound, and nonbound waters. Water molecules in dry foods are tightly bound to food molecules. Increasing tightly bound water causes a_w to rise slowly, but as loosely bound water increases, a_w increases rapidly and slowly approaches 1.0, when nonbound water increases. Crisp crackers get soggy after adsorbing water from moist air, and food dries when exposed to dry air.

Water activity affects growth and multiplication of microorganisms. When $a_w < 0.9$, growth of most molds is inhibited. Growth of yeasts and bacteria also depends on a_w. Microorganisms cease growing if $a_w < 0.6$. In a system, all components try to reach equilibrium with one another, including all the microorganisms. Every type of organism is a component and a phase of the system, due to their cells or membranes. If the water activity of an organism is lower than that of the bulk food, water will be absorbed, and thus the species will multiply and grow. However, if the water activity of the organism is higher, the organism will dehydrate and become dormant or die. Thus, it is not surprising that water activity affects the growth of various molds and bacteria. The bakery industry has already taken this into consideration in their packaging of bakery products.

Epilogue

Baking is an art, business, engineering, hobby, and science. Due to the variety of ingredients and processes, the chemistry and physics in baking are very complicated. Based on its properties, the role of water in baking is described, but the scope is wider than what has been covered in this chapter. The purpose of this chapter is to point the way toward further research, experimentation, and exploration, not to limit the perimeter of baking science.

Acknowledgments

Glossary

Acid—
a substance able to donate a hydrogen ion (or proton) in a chemical reaction; molecules of a *strong acid* give all its protons to water molecules, forming H_3O^+ ions and anions, but only a percentage of molecules of a *weak acid* such as lactic acid do so.

Acid dissociation constant—
a value, K_a, indicating the degree of dissociation when dissolved in water; the K_a of a strong acid is infinity and that of acetic acid is~0.00005.

Amphiphilic—
a property of substances such as emulsifiers that allows them to dissolve in both water and oil.

Aqueous solution—
a uniform or homogeneous mixture in which water is the major component (the solvent).

Base—
a substance that is able to accept a hydrogen ion in a chemical reaction, for example, OH^- ions accept H^+ to form H_2O; a percentage of molecules in a *weak base* accept H^+ from water, making some OH^- ions.

Base dissociation constant—
a value, K_b, indicating the degree of dissociation when dissolved in water; the K_b of a strong base is infinity and that of ammonia is~0.00005.

Boiling point of water—
the temperature (373K) at which the vapor pressure of water is exactly 1atm (101.325 kPa). This is not necessarily the temperature at which bubbles form.

Boiling point elevation and freezing point depression—
raising of the boiling temperature or lowering of the freezing temperature of a solution compared with those of pure water.

Buffer solution—
a solution whose acidity or pH changes very little upon the addition of a small quantity of acid or base.

Chemical potential—
a measure of the tendency of a compound to undergo chemical or physical reactions.

Clean Water Act (CWA)—
the Federal Water Pollution Control Act, passed by the United States in 1972 and widely known as the Clean Water Act.

Conjugate acid and base—

an acid such as nicotinic acid (niacin, $HC_6H_4NO_2$) that after donating a hydrogen ion (H^+) becomes a base, nicotinate ($C_6H_4NO_2^-$), because of its tendency to donate and accept H^+; $HC_6H_4NO_2$ and $C_6H_4NO_2^-$ form a pair of conjugate acid and base.

Critical temperature of water—
the temperature (647K, 374°C) above which water cannot be liquefied.

Dipole moment—
a measure of the polarity due to uneven distribution of charges in molecules; the dipole moment of H_2O is larger than that of NH_3.

Drinking water—
all waters used in food production, washing, processing, baking, and drinking.

Electrolytes—
acids, bases, salts, and other compounds that produce ions when dissolved in water; ions make the solution conduct electricity.

Emulsifier or surfactant—
substance whose molecules contain a group that likes water and a group that dislikes water so that it brings oil-type substances into an aqueous solution.

EPA—
the U.S. Environmental Protection Agency.

FDA—
the U.S. Food and Drug Administration.

Hard waters—
waters containing calcium, magnesium, carbonate, and sulfate ions; only Ca^{2+}, Mg^{2+}, HCO_3^-, and CO_3^{2-} ions are present in *temporary hard waters* because the ions are removed by boiling; permanent hard waters also contain SO_4^{2-} ions.

Hydrophilic substances—
water-loving substances, such as sugar, alcohol, and salt, that easily dissolve and get wet in water.

Hydrophobic substances—
water-hating substances such as gasoline, wax, oil, butter, margarine, lard, and shortening.

Infrared spectroscopy—
the study of the absorption of infrared by substances such as water.

Intermolecular interactions—
molecule-molecule attractions and relationships in the forms of van der Waals, polar-polar, polar-ion, and ion-ion attractions, as well as hydrogen bonding and covalent bonding.

Ion exchange—
a process using solid substances containing positive and negative ions to exchange with different types of positive and negative ions in a solution due to concentration differences.

Isoelectric point—
the pH of the solution at which molecules of a protein dissolved in it carry no net charge.

Isotherm—
  a plot of the water activity (another term in the glossary) versus the water content of a food.

Lipids—
  esters and fatty acids such as oil, butter, margarine, lard, tallow, and shortening.

Lone pair of electrons or electron lone pair—
  two valence electrons present in molecules such as NH_3 and H_2O that are not shared by hydrogen atoms; they differ from the two electrons that hold the H and N or O together as an H—N or H—O bond.

Microwave—
  a form of electromagnetic radiation, used in communication and in microwave food processors, with a frequency between radio waves and infrared.

Organic compounds—
  compounds containing carbon-hydrogen (C—H) bonds.

Osmotic pressure—
  the pressure that must be applied to the side of the solution to prevent the flow of pure water through a semipermeable membrane into the solution; applying a pressure to a solution to force molecules to pass a semipermeable membrane is called *reverse osmosis*.

pH—
  the negative log (base 10) of the concentration of hydrated hydrogen ions represented by $[H^+]$, $pH = \log_{10}[H^+]$.

pOH—
  the negative log (base 10) of the concentration of the hydroxyl ion represented by $[OH^-]$, $pOH = \log_{10}[OH^-]$.

Phase diagram—
  a diagram showing the temperature and pressure of phase transitions.

Phase transition—
  the conversion among solid, liquid, and gaseous states of matter; each state is called a phase.

Peptide or protein—
  a substance consisting of polymers whose long molecules are links of many amino acids.

Retrogradation or staling—
  randomly arranged amy-lose molecules in bread became orderly, causing bread to lose its freshness.

Superheating and supercooling—
  water temperature above the boiling point without the boiling phenomenon and water temperature below the freezing point without the formation of any solid.

Triple point of water—
  the temperature (273.16K) and vapor pressure (611.15 Pascal) at which ice, water, and vapor co-exist in equilibrium.

Water—
  a compound of hydrogen and oxygen, H_2O, including some isotopic species in solid, liquid,

and gaseous forms; may be present in other substances; may or may not be pure.

Water activity—
the equilibrium vapor pressure of a food divided by the equilibrium vapor pressure of pure water at the same temperature.

Water content—
total amount of water in a substance or food.

WHO—
the World Health Organization, an agency of the United Nations specializing in health matters.

Yeast food—
a formula used to improve the conditions for yeast growth and reproduction to produce an excellent fermentation.

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Note

[a] The information in this chapter has been modified from "Water and Baking," in *Handbook*

8
Yeast

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Introduction

Baker's yeast is an essential ingredient of many cereal-based products, and a fundamental element to ensure a reproducible production process and a high quality product to meet the demands of producers and consumers. Its primary role is the production and release of carbon dioxide (CO_2) gas, through the alcoholic fermentation of sugars, which develops the crumb structure and provides bread loaf volume. Yeast also contributes to the typical bread flavor (Cho and Peterson 2010), and is a nutritional complement and a functional ingredient of bread and baking products. Cereal fermentations show significant potential to improve nutritional quality and provide health effects (Poutanen and others 2009). Nutraceuticals are the fastest-growing segment of today's food industry and bread, as a dairy product, is considered an ideal vector of essential compounds. Typically, baker's yeast can be used as a protein, an amino acid or vitamin supplement, an energy booster or immune enhancer to create a commercialized health product (Mazo and others 2007; Moyad 2008). Modern yeast biotechnology has also led to the development of a huge array of specialized yeast with optimized or novel properties and added value, thus predicting a prosperous future for the baking industry.

Commercial baker's yeasts are defined as domesticated strains of *Saccharomyces cerevisiae*. Indeed, they fulfill the criteria of confined culture and continuous selection (Diamond 2002). They have been modified from wild ancestors to achieve rapid growth and a high biomass yield on molasses medium, coupled with a high rate of production gas during dough leavening (Bekatorou and others 2006). For decades, changes in its manufacturing process had a major impact on the baking industry, as reflected by reviews of early patents in this field (Gélinas 2010, 2012). A part of this review will be focused on this matter, emphasizing new trends such as modern liquid yeast technology or the use of new raw materials. Nowadays, scientific advances mean that molasses, which increases its cost yearly, could be replaced. Alternatives are cellulose wastes or cheese whey, among other waste materials (Bekatorou and others 2006). Some of them are expected to result in cheaper, cleaner, and more reliable procedures than those traditionally used for baker's yeast propagation. In addition, this technology offers a profitable use for these resources, some of which have a great pollution potential.

In future, a major biotechnological challenge in this area is the significant improvement of suboptimal traits, such as stress resistance. Baker's yeast cells are exposed to different stress conditions during propagation and baking, leading to inhibition of cell growth, cell viability, and fermentation (Shima and Takagi 2009). Consequently, our understanding of stress-protective molecules and mechanisms is fundamental to engineering stresss resistance. *Saccharomyces cerevisiae* has been widely used as a model organism for basic studies (Botstein and Fink 2011), to decipher mechanisms and to identify genes, signaling pathways. and metabolic networks involved in stress tolerance (Aguilera and others 2007; Hohmann 2009). Nevertheless, more work is needed to understand how multiple genes are interconnected and how these interactions, the so-called "systems biology" (Mustacchi and others 2006), determine the properties of yeast cells, in particular from industrial strains. Moreover, there is evidence that signaling pathways and stress responses have evolved in different organisms, including yeasts, in a niche-dependent manner (Nikolaou and others 2009; Smith and others 2010). It is clear, for example, that *S. cerevisiae* is not the best model

of stress-resistant microorganism. Non-conventional yeasts such as *Wickerhamomyces anomalus* (formerly *Pichia anomala*), *Candida glabrata* or *Torulaspora delbrueckii*, present in spontaneous sourdoughs (Almeida and Pais 1996a; Succi and others 2003; Paramithiotis and others 2010; Vrancken and others 2010), might have advantages over *S. cerevisiae* to cope with stress conditions (Hernández-López and others 2003). During the past decade, several studies have analyzed the fermentative *T. delbrueckii* yeast from both a fundamental and applied point of view (Alves-Araújo and others 2004, 2007; Hernández-López and others 2006a, 2010), and recently the complete sequencing of its genome has been carried out at the Wolfe Laboratory (Smurfit Institute of Genetics, Trinity College Dublin, Ireland) and made available (http://www.ncbi.nlm.nih.gov/bioproject/70971). This non-*Saccharomyces* yeast is therefore a promising model organism and an alternative from a technological point of view.

Baker's yeast production

Raw materials

At the beginning of the industrial manufacture of baker's yeast, cells were propagated using cereal extracts mainly from corn or rye malted grains(Gélinas 2009). However, the need for saccharification to form fermentative sugars before yeast growth and the high cost of the malt used in this process as a source of nitrogen and enzymes led to the search for alternatives, and by 1920, molasses had replaced starch-based media (Gélinas 2010). From that time, several problems dealing with nutritive composition, particularly nitrogen and micronutrients, molasses clarification, and infection had to be solved before the massive use of molasses and its widespread acceptance as a growth medium for baker's yeast propagation (Gélinas 2012). Overall, advances in these areas had positive effects on yeast yield, appearance, and stability, and helped to reduce the cost of the product. As the price of baker's yeast decreased, bakers had the opportunity to increase yeast doses in dough, reducing proofing time and allowing more control of the baking process. Molasses use was therefore a deciding factor in the birth of modern baking and in our perception of bread quality properties.

A blend of beet and cane molasses is commonly used in the commercial propagation of yeast. Sucrose is the predominant sugar, accounting for more than 40% (w/w). In addition, beet molasses contains up to 8% (w/w) raffinose (fructose-glucose-galactose), which is hydrolyzed by invertase to fructose and melibiose, the latter not being utilized owing to the lack of α-galactosidase. Molasses also provides minerals, vitamins, and some amino acids, although it needs to be supplemented with nitrogen, mainly as ammonium salts, and vitamins. Both cane and beet molasses contain harmful substances that inhibit yeast growth and baking performance, and a variable amount of suspended solids that must be cleaned. Molasses may vary significantly in quality from batch to batch, particularly in terms of sugar content. The development of biofuel as a substitute for oil has also increased the demand of molasses, raising prices and compromising availability. Ethanol production from sugar crops such as cane and beet account for about 40% of the total bioethanol produced worldwide (Mussatto and others 2010). These factors have contributed to the continuous search for new carbon sources and the renewed interest in starch-based media for baker's yeast propagation.

Fed-batch production of commercial yeast on glucose syrup derived from corn (Spigno and others 2009) or cassava (Aransiola and others 2006) has been proposed as it has no special requirements for processing and provides the lowest production costs. The use of starch for yeast propagation may also be more favorable for gassing power, stability, and yeast quality, compared with molasses (Gélinas 2012). However, the use of starch-based products like corn may draw criticism due to rising food prices. Cheap by-products such as date syrup (Al-Jasass and others 2010), whey (Ferrari and others 2001) or forestry and agriculture residues (Bekatorou and others 2006) have been also suggested. However, the use of these feedstocks usually requires chemical and enzymatic pretreatments to convert starch, lactose or cellulose to monosaccharides. The exploitation of genetically modified yeast strains (see later) has the potential to make the use of various wastes for baker's yeast production economically competitive (Prieto and others 2005). Despite this, we anticipate that due to public resistance

to this technology, molasses will remain the basic raw material for baker's yeast manufacturing.

Processes

Although processing details for the large-scale propagation of baker's yeast inevitably differ throughout the world, the principles underlying the propagation process are common to most plants. A schematic representation is shown in Figure 8.1. First, a batch of seed yeast, which will be used in the propagation and scaling-up process, must be prepared under laboratory conditions (Zamani and others 2008). Using a stock culture, the specific yeast strain is used to inoculate 1–75 l flasks containing molasses media. After 1–4 days incubation at 30 °C, this yeast seed will be used in a series of 5–6 consecutive batch and fed-batch fermenters of increasing size during the scale-up process.
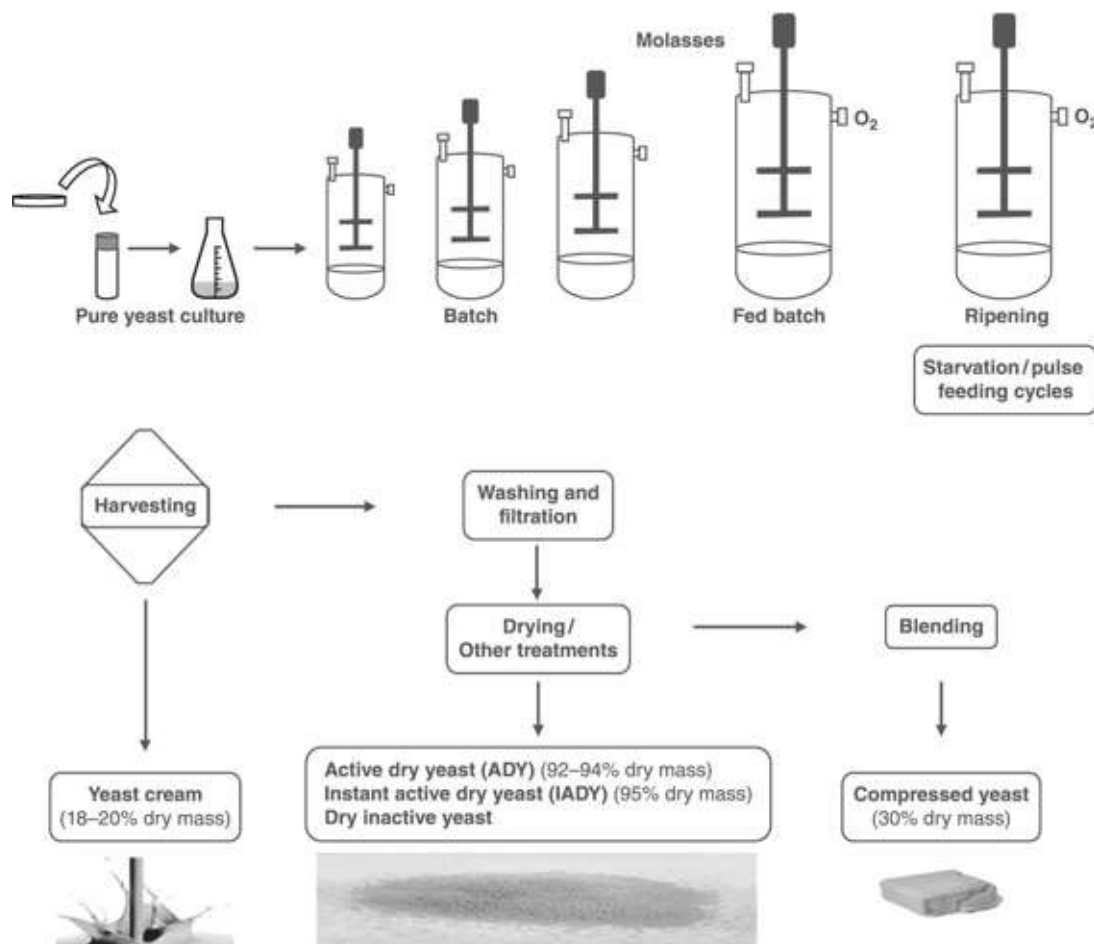
Figure 8.1 Baker's yeast manufacturing. The initial steps of the propagation process approach to pure batch culture conditions, and are such that ethanol will be formed. Then, full aeration and incremental feeding of culture medium are used to avoid sub-products production, maximizing thus, the yield of cell biomass. Finally, pulse feeding cycles are generally provided at the end of the propagation to induce the maturation or ripening of the yeast that will impart greater stability. Further processing steps include separation from the broth culture by centrifugation and washing, filtration and/or drying in order to obtain yeast cream, compressed yeast, active dry yeast, ADY, or instant dry yeast, IDY.

Propagation

In a first batch phase, the yeast produced in an earlier stage is used to seed the next stage (see

[Figure 8.1](#)), with transfer made under sterile conditions (Deák 2003). The pure culture fermenters (50–400 l) are filled with molasses conveniently diluted, clarified, sterile, and supplemented with the necessary adjuncts and growth factors (Gélinas 2012). Aeration with filtered air is not at full capacity, so ethanol may be formed to a certain extent at this stage (Rández-Gil and others 1999; Deák 2003). Additionally, excess sugar (> 0.01%) in the beginning of the batch stages, leads to a shift of the yeast metabolism called the Crabtree effect (see later Growth rate and biomass yield). This describes the phenomenon whereby *S. cerevisiae* produces ethanol aerobically in the presence of high glucose concentrations rather than producing biomass via the tricarboxylic acid cycle (Thomson and others 2005). Despite this, the batch phase ensures the accumulation of important reserve metabolites in the cells (Pérez-Torrado and others 2009) and avoids a partial loss of glycolytic capacity such as that observed after prolonged glucose-limited aerobic growth (Jansen and others 2005). Finally, the presence of O_2 allows yeast to oxidize the produced ethanol when sucrose is exhausted, which triggers the switch from fermentation to respiration (Pérez-Torrado and others 2009; Gómez-Pastor and others 2011).

The second phase involves 2–3 fed-batch fermenters (see [Figure 8.1](#)), where nutrients and molasses are incrementally fed through a circulation loop in cycles lasting 11–15 h. At this stage, it is essential to control and optimize, as much as possible, all the factors that govern the yeast respiration metabolism. Maximum aeration is supplied to the tanks to increase the dissolved oxygen, which also depends on sugar, biomass concentration, temperature, and pH. In this sense, several mathematical models have been proposed to predict dissolved oxygen (Blanco and others 2008), as well as biomass (Hocalar and others 2011), over time. Nitrogen sources, usually from inorganic supplements, must be sufficiently provided to yield the maximum biomass, and sugar concentration must be below 0.01% to prevent ethanol formation. This depends in part on designing factors as in the commercial scale bioreactors ($100–400 \ m^3$), the complete nutrient distribution is not fully guaranteed (Devarapalli and others 2009). For example, increased sugar concentration at the feeding point, simultaneously promotes alcohol formation and alcohol consumption, reducing the theoretical biomass production from 0.50 to 0.39 g per gram of glucose. However, it has been reported that a higher local sugar concentration in the circulation loop results in a better leavening ability and shelf-life for the same biomass yield of the final product (Zamani and others 2008). In addition, it is thought that this phenomenon allows enhanced glycerol production (Myers and others 1997), with the corresponding yeast performance improvement on sugar dough (George and others 1998). On the other hand, more recent studies show that stress conditions during the propagation process, such as oxidative stress or starvation/pulse feeding cycles, can enhance the dough leavening activity of yeast (Galvagno and Cerrutti 2004; Pérez-Torrado and others 2009).

At the end of this stage, feeding is stopped and aeration is continued for 0.5–1 h. This ripening sequence allows yeast cells to complete their reproduction cycle and form carbohydrate reserves due to the reduced rate of protein synthesis (Deák 2003). Overall, this phase will help yeast cells to survive starvation during subsequent storage at low temperatures and to be ready to form large amounts of gas in the hydrated but microaerophilic conditions of bread dough.

Concentration and conditioning

The culture medium at the final bioreactor, containing about 5–6% yeast (dry weight), is centrifuged, and a water wash is applied between two passages through centrifugal separators. The cleaning process removes impurities that could affect the color or hydration properties of the final commercial products (Rose and Vijayalakshmi 1993) and facilitates further concentration (see Figure 8.1).

Liquid and compressed yeasts

A yeast cream is obtained after centrifugation and cleaning with 18–20% dry weight, which can be stored in agitated tanks at 2–4 °C for a few days without any loss of quality and for a maximum shelf-life of about 3 weeks (Beudeker and others 1990). The use of cream yeast avoids post-processing steps and offers several advantages. Contrary to compressed yeast, liquid yeast may be mixed, pumped, and measured by volume or weight, and consequently, is the preferred choice for highly automated bakeries (Gélinas 2010). Furthermore, the liquid yeast can be directly mixed with bread improvers to avoid separate weighing of these ingredients, and is helpful for standardizing gassing power, which may vary from batch to batch, allowing a more accurate and cost-effective dosing (Gélinas 2010).

Despite this, compressed yeast is the traditional form in which baker's yeast is sold and used in bakeries. For its preparation, small quantities of oils (like soy oil) and emulsifiers are added which improve extrusion and provide a white creamy appearance. The cream is filtered to give a thick paste which is then extruded through a screen to continuous threads to be subsequently cut in pieces. Compressed yeast has a moisture content of 27–34% and a protein content of 42–56% (Beudeker and others 1990). It is ready for immediate use and its shelf-life is equal to liquid yeast (3–4 weeks) under refrigeration temperatures, with only a slight decrease in leavening activity over time (Deák 2003). If improperly wrapped or refrigerated, compressed yeast can rapidly dry out or run out of carbohydrate reserve, resulting in a rapid loss of activity.

Dry yeast

Instead of being cut after extrusion, the compressed yeast may bechopped up and dried (see Figure 8.1) to obtain the two main forms of dried yeast: active dried yeast (ADY) and instant dried yeast (IDY), both of which contain 6–8% moisture and 40–43% protein (dry weight, basis). Under optimal conditions, dry yeast shows the same leavening activity of compressed yeast and a shelf-life under vacuum of at least one year at room temperature (Deák 2003). However, drying, storage, and later rehydration impose extreme stress conditions to yeast cells, including water, thermal, and oxidative stress, that cause cellular damage and loss of viability. Leakage of cell constituents, among them glutathione, can also alter the technological properties of flour, weakens gluten, and limits dough expansion and bread volume (Rose and Vijayalakshmi 1993).

Due to these issues, dry yeast preparation requires a specific propagation process and the use of drying-tolerant strains. Low nitrogen supply, about half-way during the final stage, decreases the content of certain lytic enzymes, minimizing breakdown during dehydration (Rose and Vijayalakshmi 1993). At the same time, carbohydrate accumulation is promoted (for example trehalose), offering additional protection during drying. Before yeast extrusion, emulsifiers such as sorbitans, known as Span, citric acid esters of monodiglycerides, and polyglycerol esters are frequently used to facilitate rehydration of the yeasts in dough.

Rehydration at 40 ℃ is also recommended to maintain a critical fluidity of the plasma membrane and minimize leakage of cell constituents and subsequent loss of viability.

With the same idea, important efforts have been dedicated to develop more friendly and efficient drying processes. Indeed, in the ADY process, yeast cells are dried in a belt dryer for 2–4 h at 25–45 ℃, while the most recent IDY process make use of a fluidized bed at up to 150 ℃ for 0.5–2 h. The yeast is presented as small rods with a granulation size of 0.2–0.6 mm. The rods' high porosity allows for immediate use without the need for rehydration and they can be mixed directly with flour in making dough (Deák 2003). Nevertheless, the complex and sophisticated production of dried yeast, especially IDY, significantly increases production costs, which has limited its expansion in the yeast market. Thus, several changes have been proposed to optimize energy consumption (Köni and others 2009), as well as operational conditions (Akbari and others 2012).

Other yeast products

A minor but profitable use of baker's yeast is in the manufacture of various kinds of yeast derivates (http://www.yeastextract.info/), including inactive yeast, yeast autolysates, yeast hulls or walls, and yeast extracts (Pozo-Bayón and others 2009; Alexandre 2011).

Commercial inactive yeast is a product without fermentation ability, used for the conditioning of dough properties or the development of increased aroma (Pozo-Bayón and others 2009). Thermolysis renders the yeast cell inactive, and it is spray-dried into a fine powder that has slight yeasty and meaty flavors. It is a highly digestible and nutritious food, containing more than 50% of protein, minerals, and vitamins (Bekatorou and others 2006).

Yeast extract consists primarily of amino acids, peptides, nucleotides, and other soluble components of yeast cells (Chae and others 2001). It has been mainly used in the food industry as a flavoring agent, but also has applications as a source of vitamins and proteins in food supplements or as an ingredient in microbiological media (Bekatorou and others 2006; Milić and others 2007). There are three main methods for the production of yeast extract: autolysis, plasmolysis and hydrolysis. The most frequently used manufacturing practice is autolysis, which is essentially a degradation process carried out by the yeast's own enzymes, in conditions of controlled temperature and pH (Alexandre 2011; Comuzzo and others 2012). As flavor bases, yeast extracts are blended and mixed with amino acids and sugars to promote, through the Maillard reaction, more specific baked flavor notes to be used in muffins, shortbread biscuits or cookies.

Lastly, cell walls are the non-soluble fraction obtained as a co-product of the yeast extract process. After yeast is autolysed, the insoluble cell walls are separated from the soluble yeast extract by centrifugation and then spray or drum dried. They are clean label ingredients which provide: high water-holding and food thickener activities, carrier for flavors and a source of yeast dietary fiber (β-glucans). In addition, cell walls fractions can be isolated from whole ADY or isolated walls, and used for specific purposes. For example, mannoproteins (25–50% dry weight) can be used to improve ADY rehydration or the sensory characteristics of wines (for example color stabilization of red wines) (Pozo-Bayón and others 2009), although most cell wall components are intended for manufacturers in the field of food/dietary supplements and functional foods. Beta-1,3/1,6-glucan contributes to the proper functioning of the immune system, while glucomannans extracted by centrifugation of cell debris have been shown to act as a biological response modifier.

Technological needs

The development by the yeast industry of suitable growth media and changes in the manufacturing process have had a major impact on yeast yield, color, gassing power, and stability. The improvement of these technological traits has been critical for improving the acceptability of commercial baker's yeast by the baking industry. Nowadays, yeast producers face new challenges from the latesttechnology trends in baking and the need to reduce costs and increase yield.

Growth rate and biomass yield

Easily fermentable monosaccharides such as glucose or fructose are clearly preferred by *S. cerevisiae*. In its presence, the main glucose repression pathway downregulates the expression of several genes involved in the uptake and metabolism of alternative carbohydrates, as well as genes involved in respiration (Crabtree effect, see earlier Propagation section) and gluconeogenesis (Thomson and others 2005; Gancedo 2008; Busti and others 2010). As a result, this regulation ensures that glucose is consumed before other carbon sources (that is maltose) and prevents the generation of futile cycles by shutting down the gluconeogenic pathway. However, the glucose repression mechanism has negative effects on biomass production.

As mentioned earlier (see Propagation section), maximization of biomass yields is hampered by the tendency of baker's yeast cells to produce ethanol when sugars are present in excess, even under aerobic conditions. This ethanol formation can be limited by growing yeast cells under conditions of low sugar feeding (Valentinotti and others 2003). In addition, several strategies to modify the carbon flux to favor respiration over alcoholic fermentation have been explored. Decreasing the expression level of fermentative enzymes was not successful, due to its negative effect on growth (Flikweert and others 1999). As an alternative, increasing the yeast respiratory activity seems a more reliable option. In fact, cells overexpressing the Hap4p activator subunit of the Hap2/3/4/5 transcriptional complex, which is involved in the glucose-dependent regulation of the respiratory status, showed an impaired production of ethanol and glycerol, and a 40% gain in biomass yield (Blom and others 2000). When this strategy was carried out in commercial baker's yeast, a slight improvement in biomass yield was obtained (5−9%) and these strains showed a dough fermentation capacity comparable to their parental counterpart (Dueñas-Sánchez and others 2010).

Similarly, combined deletion of *MIG1* and *MIG2*, the two main glucose-transcriptional repressors in *S. cerevisiae* (Busti and others 2010), has been successful in alleviating glucose control with respect to sucrose metabolism. Alternatively, a derepressed yeast strain has been obtained by constitutive activation of the protein kinase Snf1, which is the main regulator of glucose derepression in *S. cerevisae* (Busti and others 2010). This modification led again to the upregulation of glucose-repressed genes, a decrease in by-product formation (ethanol and glycerol), and an increase in biomass yield (Raab and others 2011).

Fermentative performance

Although yeast propagation requires the suppression of alcoholic fermentation, the primary

role of yeast in the bread making process is the production of CO_2. Therefore, the balance between fermentation and respiration must be carefully controlled during yeast manufacturing to obtain high biomass yield accompanied by optimal fermentation performance during downstream applications. For instance, the combination in industrial propagation media of sucrose from molasses with maltose syrups or with non-fermentable carbon sources (mannitol or sorbitol) has been reported to increase the level of storage carbohydrates, improving stress resistance and fermentation rates (Verstrepen and others 2004). Nevertheless, as already mentioned (see earlier Raw materials section), maltose- or starch-based feedstocks are essentially food, and this compromises its use. On the other hand, the polyols mannitol and sorbitol are extremely expensive, and thus, attempts to increase the fermentative capacity of baker's yeast by molecular approaches should be considered.

In the past, it was suggested that the alcoholic fermentation could be increased by overexpressing key enzymes of the glycolytic pathway. Such an approach failed, however, to yield the expected results (Schaaff and others 1989), because a metabolic flux is hardly ever controlled by a single enzyme and the overproduction of all enzymes of the pathway is questionable (van Maris and others 2001). Another approach has been the modulation of the glycolysis–gluconeogenesis balance by the introduction of futile cycles. For that, *FBP1* and *PCK1*, the genes encoding the gluconeogenic enzymes fructose-1,6-bisphosphatase and phosphoenolpyruvate carboxykinase, respectively, were put under the control of a promoter non-repressible by glucose. The resulting strain showed a 35% gain in CO_2 production, but as expected, a significant reduction in biomass yield (Navas and others 1993), making this approach uneconomic.

A much more successful idea has involved the optimization of maltose use. Wheat flour is composed mainly of starch and free sugars (maltose, sucrose, glucose, fructose, and glucofructans). Maltose is the most abundant sugar due to its release from starch during the baking process by the activity of flour amylases. Efficient fermentation of maltose is limited by both glucose-repression and glucose-inactivation of maltose-utilizing enzymes. As a consequence, a lag phase in CO_2 production is observed that increases the fermentation time (Higgins and others 1999). Several strategies have been designed to avoid this lag period, including the construction of a baker's yeast strain with constitutive expression of maltase and maltose permease genes (Rández-Gil and others 2003) or the isolation of naturally occurring mutants insensitive to glucose-repression (Rández-Gil and Sanz 1994; Rincón and others 2001; Salema-Oom and others 2010).

Stress resistance

Stress resistance is a desirable trait of industrial microorganisms because either biomass production processes or downstream applications expose them to a simultaneous or sequential combination of different environmental stresses (harmful conditions). Baker's yeasts are not immune to this situation, particularly because *S. cerevisiae* is rather sensitive to common stresses such as ionic, thermal, or oxidative stress (Aguilera and others 2007; Hohmann 2009). It is noteworthy that other microorganisms, and specifically stress-tolerant non-*Saccharomyces* yeasts isolated from sourdough, have been considered as good candidates to improve the fermentative performance of, for example, sweet or frozen-dough (see later section). Nevertheless, *S. cerevisiae* baker's yeasts are still the first choice in

baking, and efforts have been made to select and engineer more robust yeast strains, with tailored properties for each particular end-use.

Osmotolerance and ion toxicity resistance

The so-called sweet goods, such as Danish pastry, doughnuts, croissants, and Viennese bread, contain up to 40% added sucrose or glucose/fructose syrup as a sweetening agent, often combined with fat, powdered milk, and salt. As a result, yeasts are exposed to low water activity and high levels of toxic Na^+ and Cl^- ions, which cause loss of fermentation capacity, leading to longer proofing times and reduced product volume (Hernández-López and others 2003). Thus, the ability of yeast to withstand increasing osmotic pressures is a key point in the baking process, and improvement of yeast osmotolerance has become a major focus of attention.

Several approaches have been explored to select yeasts with improved behavior under osmotic stress conditions. A schematic overview is shown in Figure 8.2. Initial attempts were focused on industrial strains with low invertase activity ("slow" strains), which alleviates the high osmotic pressure resulting from the hydrolysis of sucrose into glucose and fructose. Nevertheless, these strains do not show intrinsic osmotolerance and at higher sugar contents the osmotic pressure inhibits their activity (Hernández-López and others 2003). Improvements have also emphasized in the role of glycerol as osmoprotector. Studies on the osmotic response of different baker's yeast strains showed a positive correlation between overproduction of glycerol and fermentative performance in high sucrose dough (Attfield and Kletsas 2000). Therefore, different pretreatments have been suggested to obtain cells with high polyol content for baking applications (Hirasawa and Yokoigawa 2001). Nevertheless, these methods are laborious, difficult to apply in the baking practice, and sometimes expensive.
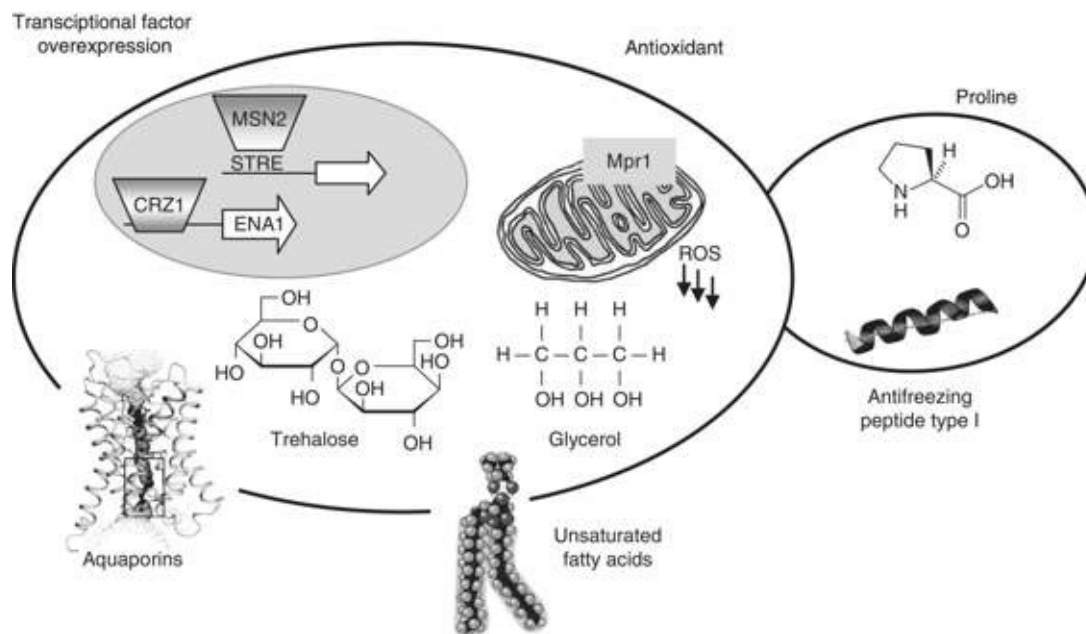
Figure 8.2 Overview of molecular approaches to endow baker's yeast cells with increased osmotic and freeze tolerance. Resistance to freezing has been reported in cells that accumulate higher levels of protective molecules such as glycerol, proline or trehalose, or that overexpress the *AQY2* aquaporin-encoding gene, involved in water efflux, or *MPR1*, the yeast N-acetyltransferase. Successful results have also been obtained by producing recombinant anti-freezing peptides or increasing the unsaturation index of the *S. cerevisiae* membrane. Likewise, enhanced stress resistance has been reported by overexpression of transcription factors involved in the regulation of stress-related genes.

In a different approach, metabolic engineering of glycerol production has been followed using different strategies (Bell and others 2001; Rández-Gil and others 2003). Unfortunately, altered intracellular glycerol levels seem to have dramatic effects in other metabolic branches (Remize and others 2001), as could be expected from the multiple functions of the glycerol pathway in *S. cerevisiae* (Hohmann 2009). In addition, rerouting carbon flux to glycerol biosynthesis could also have negative effects on the other by-products of alcoholic fermentation, such as ethanol and especially CO_2 (Remize and others 1999). Nevertheless, different genetic engineering approaches seem to have been more useful. For instance, overexpression of *CRZ1*, the main transcriptional factor in the salt-stress yeast response (Yoshimoto and others 2002; Cyert 2003), increased NaCl tolerance and improved the leavening ability of baker's yeast in high-sugar dough (Panadero and others 2007).

Cryoresistance

In the baking industry, frozen-dough technology has been widely extended as it has several advantages over fresh products. Frozen dough can be distributed and baked on-demand at the point of sale or consumption. In addition, it improves labour conditions for bakers. With the appropriate ingredients, formulation, low-temperature mixing, and deep freezing technology, a long shelf-life can be achieved, which is only limited by a progressive decline in dough proofing power (Loveday and Winger 2007; Yi and others 2009). This drawback is caused to two factors: (i) a loss of dough gas retention ability, and (ii) diminished yeast activity (Loveday and others 2012).

It is difficult to associate freezing cell damage to a particular stress. Evidence suggests that freezing is a complex and multifaceted stress, in which different stressors and stress

responses seem to play important roles (Aguilera and others 2007). Ice formation outside cells concentrates the surrounding solution producing hyperosmotic stress (Wolfe and Bryant 1999). Hence cells dehydrate by outward movement of water or intracellular freezing due to internal nucleation, depending on freezing rate (Loveday and others 2012). Mechanical stress resulting from ice crystal growth during frozen storage can further deteriorate cell structures, in particular the plasma membrane. Finally, during the thawing process, cells might be exposed to oxidative stress and initiate their fermentative activity, increasing freeze sensitivity (Loveday and others 2012). It is not surprising, therefore, that freezing tolerance involves various mechanisms and that different approaches have been followed to provide increased frozen dough performance (see [Figure 8.2](#)).

Resistance to freezing by mitigating the effects of osmotic stress has been reported. Yeast strains that accumulate higher levels of protective molecules such as glycerol (Izawa and others 2004a, 2004b), proline (Terao and others 2003; Kaino and others 2008) or trehalose (Shima and others 1999), or that overexpress the *AQY2* aquaporin-encoding gene, involved in water efflux (Tanghe and others 2002), have shown increased survival after freezing–thawing and/or preserved proofing power in frozen dough applications. Of these, the best results have been obtained by manipulating the pathways for proline and nitric oxide biosynthesis. Thus, construction of a self-cloned diploid baker's yeast strain which overexpress active alleles of *PRO1*, encoding for γ-glutamyl kinase, and *MPR1*, the N-acetyltransferase, increased the tolerance to freezing, but also to multiple baking-associated stress conditions, including air-drying and, as could be expected, hyperosmotic stress (Sasano and others 2012a). Simultaneous accumulation of proline and trehalose have also been followed by expressing a proline-feedback inhibition-less sensitive allele of *PRO1* and disrupting the *NTH1* gene, encoding neutral trehalase (Sasano and others 2012b). Interestingly, characterization of the resulting strain suggests that proline and trehalose protect yeast cells from short-term and long-term freezing effects, respectively.

Other targets of freeze damage have also been considered. For example, Panadero and others (2005) reported the construction of a baker's yeast strain able to produce the recombinant antifreeze peptide GS-5, which displays the ability to inhibit the growth of ice during frozen storage. As a result, the recombinant yeast cells exhibited increased gassing rate and total gas production in frozen and frozen sweet dough (Panadero and others 2005). The protective effect of unsaturated lipids on membrane fluidity transitions (Aguilera and others 2007) has also been explored. Indeed, alteration of the unsaturation index of the *S. cerevisiae* membrane, through the heterologous expression of sunflower desaturase genes, increased the tolerance to freezing stress (Rodriguez-Vargas and others 2007). Lastly, several authors have explored the possibility of enhancing freeze tolerance by increasing the yeast cell stress responses. Examples of this strategy are mainly based on the observation that the freeze–thaw response of yeast is mediated by the RAS-cAMP pathway (Park and others 1997; van Dijck and others 2000; Teunissen and others 2002). Consistent with this, a study by Sasano and others (2012c) engineered the transcription factors Msn2p/Msn4p, which control the general stress response in *S. cerevisiae*, through the RAS-cAMP pathway (Estruch 2000). Thus, a self-cloning baker's yeast overexpressing *MSN2* showed increased proofing power in frozen dough (Sasano and others, 2012c). In other research, Pérez-Torrado and others (2010) demonstrated that the overexpression of *CAF16* and *ORC2*, two transcriptional factor-encoding genes differentially regulated in sweet dough, confers ion and freeze tolerance in this condition, improving leavening activity in frozen high-sucrose dough. Hence, engineering

of genes with regulatory functions has emerged as a successful strategy for improving industrial baker's yeast strains.

Extension of substrate range

As mentioned earlier, the use of wastes and by-products other than molasses for the production of yeast biomass had been traditionally considered as uneconomic. Indeed, the lack in *S. cerevisiae* of an adequate enzyme repertoire to break down oligosaccharides and carbohydrate polymers, and its inability to utilize xylose, the major pentose sugar found in agricultural wastes, are main problems for extending the range of substrates in the yeast industry. Nevertheless, the introduction of engineered strains and the increasing concerns about the use of molasses have renewed the interest of yeast producers in alternative carbon sources and raw materials.

Yeast biomass can be produced from the enzymatic conversion of lactose, starch or lignocelluloses, into hexoses such as glucose or galactose (Rández-Gil and others 2003; Adam and others 2004; Bekatorou and others 2006). Lactose is the main constituent of cheese whey, an interesting growth medium for biomass production, due to the large amounts of whey surplus generated globally (Rubio-Texeira 2006; Domingues and others 2010). Efficient Lac$^+$ *S. cerevisiae* strains have been constructed by heterologous expression of *LAC* genes from different species (Rubio-Texeira and others 2001; Guimarães and others 2008). Interestingly, this strategy has been also followed to accomplish dough fermentation with whey-grown biomass. Recombinant baker's yeast, carrying multiple copies of the *Kluyveromyces lactis* genes *LAC12* and *LAC4*, displayed a high growth rate, biomass yield, and similar baking properties to molasses-grown commercial baker's yeast (Adam and others 1999).

The use of starch and lignocellulose requires thermal pretreatment and enzymatic hydrolysis, which in turn involves the use of thermostable bacterial or fungal enzymes (Robertson and others 2006). For cellulose and hemicellulose, the polymers must be extracted and separated from other lignocellulosic materials in a series of conditioning steps (Liu and others 2011; Peng and others 2012). A number of issues have been identified in these processes, including excessive energy demands, high enzyme requirements and cost, incomplete conversion, and no less important, the Xyl$^-$ phenotype of *S. cerevisiae*. Significant reductions in the process energy may be achieved through the use of advanced isolation and purification strategies (Peng and others 2012), or by raw starch digestion (Robertson and others 2006). Opportunities to reduce costs also make use of enzymes produced *in situ* by *S. cerevisiae*. Genetically engineered strains capable of producing different starch-degrading (Rández-Gil and others 2003), cellulose-degrading (Liu and others 2011) and hemicellulose-degrading (Peng and others 2012) enzymes have been successfully constructed. *S. cerevisiae* strains capable of rapid growth and fast xylose consumption producing only biomass and negligible amounts of by-products have been obtained by recombinant technology and adaptive evolution (Scalcinati and others 2012). Nevertheless, the use of these recombinant strains must be tested under baking conditions to ensure that the heterologous enzymes have no undesirable effects on dough rheology and bread quality.

Yeast selection and strain development

The yeast *Saccharomyces cerevisiae* has been exploited by humans for millennia to ferment and preserve food and beverages, and their genetic diversity is strongly connected to human history (Legras and others 2007). It is believed that fermentation technology expanded from Asia, Mesopotamia, and Egypt throughout the Old World. However, the emergence of yeast-raised bakery products, its geographic expansion and evolution, and the effects of human history on baker's yeast diversity still remain unclear. Recent studies suggest a positive correlation between the genetic characteristics of *S. cerevisiae* strains and their specific use for food-production (Fay and Benavides 2005; Legras and others 2007), leading to the hypothesis that the use of a yeast strain in a specific fermentation process, determine its domestication. Thus, baking technology has contributed to the genomic constitution of industrial baker's yeast, which in turn, has influenced modern baking practice.

Genetic characteristics

Industrial yeasts are domesticated strains of *S. cerevisiae* that have been selected by cross-breeding in captivity and optimized under selective conditions for specific applications (Diamond 2002). As a result, they comprise a genetically diverse collection of strains, with specific genomic signatures that define each industrial class of yeast (Liti and others 2009; Warringer and others 2011; Borneman and others 2011). For example, ale strains share the *RTM1* cluster, which has been involved in resistance to an inhibitory substance found in molasses (Ness and Aigle 1995). This genetic variation thus comprises both single nucleotide polymorphisms and large-scale insertions and deletions that determine ORF heterogeneity between strains (Dequin and Casaregola 2011). In addition, industrial yeasts are diploid, triploid, tetraploid, polyploid, and some are aneuploids. Modifying the dosage of some important genes could be a way for yeast to adapt to the various environments (Rández-Gil and others 2003). A high level of karyotype polymorphism has also been observed, resulting from various mechanisms such as mitotic or ectopic recombination mediated by Ty transposons (Puig and others 2000) or other repetitive sequences (Ness and Aigle 1995). All these mechanisms confer variable sporulation ability – ranking between high frequency (>50%) to zero sporulation rates – and spore viability (Attfield and Bell 2003; Magwene and others 2011).

A comparative study of industrial yeasts, has shown that baking strains are heterothallic (switch mating type rarely if at all) and tetraploids, specifically display four complete chromosome sets arising from the same species (Albertin and others 2009). Specifically, it has been proposed that actual bread yeast strains could originate from a tetraploidization event between an ale beer and a wine strain. This suggestion could explain the presence in bread strains of a combination of alleles intermediate between beer and wine strains (Legras and others 2007). In addition, these tetraploid strains display four alleles at several microsatellite loci, suggesting again that they only have *S. cerevisiae* ancestors. In agreement with this, karyotype analysis and RFLP markers identified *S. cerevisiae* strains and excluded interspecific hybrids. The analysis of marker segregation revealed tetrasomic inheritance at meiosis, giving additional evidences for autotetraploidy (Albertin and others 2009). This is in some way surprising since domesticated industrial yeast has the tendency to evolve towards

diploids or haploids with improved fitness (Andalis and others 2004; Gerstein and others 2006, 2008; Aguilera and others 2010). One plausible explanation is that human selection has maintained this polyploidy.

Thus, the selection by producers for broad yeast traits, such as robustness, growing rate or fermentative capacity, which all favored a high ploidy level, would have contributed to this feature. This is supported by several experimental data. Industrial yeasts show higher levels of glycolytic enzymes than wild type strains (van Hoek and others 2000). Dough-leavening ability also correlates with a high activity of the *MAL* genes (Higgins and others 2001), which determines the capacity of maltose transport and hydrolysis. Increasing the number of chromosomes will therefore raise the copy number of favorable genes leading to strains with enhanced fitness, increased maltose utilization capacity or increased vigor (Adams and others 1992; Bell and others 2001).

Yeast selection

Traditionally, strain improvement has been carried out by random mutagenesis and selection or high-throughput screening. Mating and hybridization are also useful technologies for this purpose (Attfield and Bell 2003; Nevoigt 2008). Nevertheless, in past decades, metabolic engineering became the most popular technology (Nielsen 2001; Raab and others 2005), because it allows the modification of one specific trait without the accumulation of unfavorable changes in industrial strains. Moreover, the introduction of foreign genes into *S. cerevisiae* has endowed novel capabilities and increased technological performance. Examples of this have been given in the Technological needs section of this chapter. In 1996, Bailey and co-workers introduced the concept of reverse metabolic engineering to the field of biotechnology, which is depicted as one of the major driving forces for the genetic improvement of industrial yeast strains in the coming decade.

Mutagenesis

The use of mutagenesis by ultraviolet irradiation or chemical mutagens such as ethyl methane sulfonate, followed by a screening or selection procedure, is an efficient approach to improve yeast strains. This method does not require any knowledge of target genes or metabolic pathways and is relatively easy to perform. Although, the ploidy of industrial strains imposes the need for mutation of more than one gene copy to detect changes in the phenotype, it is relatively easy to find dominant mutations. However, a disadvantage of this methodology is the relatively high frequency of generating deleterious gene alterations.

Mating and hybrid construction

Strain improvement of industrial microorganisms is rarely based on traditional breeding, either because the number of genes involved in conferring a desired characteristic is unknown, they are difficult to manipulate (as explained before), or they lack a sexual cycle. Mating programs can be direct or random. Indirect programs, selected spores that carry different desirable traits are mated. Two approaches are used in random mating: mass mating (thousands of mating type strains are mixed without prior screening) and rare mating (one industrial strain, of unknown mating type, is force-mated with known mating type strains). In both random or direct mating, generated hybrids must be selected from unmated cells. Taking into consideration that spores derived from commercial strains are prototroph, the

use of standard complementary genetics is not possible if we do not generate those strains before starting the mating program. Interestingly, strains obtained by mutagenesis or mating are not considered as GMOs, and thus, they could be transferred to the industry. Two other strategies, protoplast fusion and cytoduction, were extensively used to obtain diploids, intraspecific breeding, and so on (Pretorius 2000; Hansen and Kielland-Brandt 2003), but the resulting strains are considered GMOs. Out of this, highly efficient screening procedures need to be afforded to select an improved strain with the desired phenotype.

Genetic engineering

Classic selection and breeding methods are not specific enough to modify a single property without compromising other important characteristics of industrial strains. Thus, genetic engineering, a discipline thatemerged in the early 1990s, has played an exceptional role in yeast strain improvement. It is difficult to define metabolic engineering, but nowadays it is seen as an iterative process including several rounds of engineering, analysis, and modeling of metabolic fluxes (Nielsen 2001; Raab and others 2005). Other engineering disciplines such as inverse metabolic engineering or evolutionary engineering have appeared recently to facilitate rational metabolic engineering. The aim of rational metabolic engineering is to modify enzymes, transporters, or regulatory proteins based on available information about the pathways, enzymes, and their regulation. Although this approach has led to the improvement of many industrially relevant traits, some attempts failed, were less successful than predicted, or produces unwanted side effects (Pretorius 2000; Dequin 2001; Pérez-Torrado and others 2010).

Inverse metabolic engineering

To overcome the limitations of rational metabolic engineering, an alternative strategy was defined. In this approach, the starting point is the identification, isolation (from nature or culture collection) or creation (random mutagenesis or introduction of gene libraries) of an existing strain with improved performance relative to the reference strain (Alper and others 2006; Hughes and others 2012). The next step is to identify the genetic basis for the differing trait values. Global methods of gene expression analysis (transcriptomics, proteomics, metabolomics, fluxomics, and genome-sequencing) are powerful tools to establish a correlation between an industrially relevant trait and the expression levels of individual genes. This correlation could be used to design strategies of rational metabolic engineering in the same strain (or in another), and verify its contribution to the observed phenotype. Several examples of its application haven been revised recently (Oud and others 2011).

Evolutionary engineering

When the desirable phenotype is complex and involves many genes or more than one pathway, evolutionary strategies for the selection of these strains appear as more advantageous. This method exploits "natural design principles", thus, applying culture conditions that provide an appropriate selection pressure, favors the growth of mutants within the evolving population with the desired phenotype (Sauer 2001; Cakar and others 2012). There are a number of examples illustrating the power of this approach pointing out their success in the development of stress-resistant industrial strains (Cakar and others 2005; Aguilera and others 2010; Cadière and others 2011; Kutyna and others 2012).

Non-*Saccharomyces* baker's yeast

Research efforts have recently been directed towards the characterization of yeast communities associated with traditional fermentations (Verdugo-Valdez and others 2011). It is now generally accepted that many of the so-called non-*Saccharomyces* yeast species, have the potential to survive and proliferate under specific environmental conditions (Kurtzman 2011). Their unusual metabolic activities and their metabolites can facilitate the fermentation processes and impart distinct desirable characteristics to the final products (Jolly and others 2006). A clear example is the increasing popularity of sourdough fermentation due to its beneficial effects on organoleptic, nutritional, and health-promoting properties (De Vuyst and Neysens, 2005; Hansen and Schieberle 2005). Studies on sourdough yeast biodiversity have established the dominance of species of different genus, including *Wickerhamomyces, Candida* or *Torulaspora* (Almeida and Pais 1996a; Succi and others 2003; Paramithiotis and others 2010; Vrancken and others, 2010).

The ascomycetous yeast genus *Torulaspora* is closely related to the genera *Saccharomyces* and *Zygosaccharomyces* (Kurtzman 2003) and includes at least six species viz. *T. delbrueckii, T. pretoriensis, T. franciscae, T. globosa, T. maleeae*, and *T. microellipsoides* (Kurtzman 2011). From them, *T. delbrueckii* has been identified as one of the most abundant non-*Saccharomyces* species present in home-made corn and rye bread dough (Almeida and Pais 1996a). It is also frequently found in alcoholic beverages, fruit juices and high-sugar-containing foods (Esteve-Zarzoso and others 2001), often being considered as a spoilage yeast (Schuller and others 2001). Nevertheless, *T. delbrueckii* strains have been selected and are currently used to improve flavor and other sensory properties in wine production (Jolly and others 2006; Bely and others 2008; Renault and others 2009). High fermentation efficiency, osmotolerance, and freeze resistance properties have also made this non-*Saccharomyces* yeast the most promising alternative to industrial *S. cerevisiae* baker's yeast strains (Hernández-López and others 2003).

Metabolic and physiological analyses of *T. delbrueckii* strains have begun to establish the mechanisms underlying the ability of this yeast to proliferate in dough environments. The results have shown that both maltase and maltose transport in *T. delbrueckii* are subject to glucose repression and maltose induction (Alves-Araújo and others 2004). Nevertheless, glucose control over maltose metabolism was stricter in *T. delbrueckii* (Alves-Araújo and others 2005), and thus, this yeast showed a higher contribution of respiration compared with *S. cerevisiae* (Alves-Araújo and others 2007). Indeed, under oxygen-limited conditions, such as those found in bread dough, the increase in fermentation ability of *T. delbrueckii* was less pronounced than that of *S. cerevisiae* (Hanl and others 2005). Overall, this behavior could represent an asset for the large-scale production of *T. delbrueckii* (Alves-Araújo and others 2007). For the baking process, however, it means an undesirable delay in CO_2 production from maltose and lower leavening activity as compared with that observed for *S. cerevisiae* (Alves-Araújo and others 2005), that could be only counteracted by the exceptional ability of *Torulaspora* cells to cope with several stresses.

The leavening activity of *T. delbrueckii*, strains IGC5321 and IGC5323 (Almeida and Pais 1996a), was greater than that of *S. cerevisiae* in bread dough containing 20% sucrose and 2% added salt (Hernández-López and others 2003). In addition, the effect was more pronounced in frozen dough, in agreement with the reported freeze-tolerance of this yeast (Almeida and

Pais 1996b). These traits correlated with a low invertase activity, a slow rate of trehalose mobilization, and the ability to respond rapidly to osmotic stress (Hernández-López and others 2003). Growth behavior on high osmotic synthetic media was also examined. Cells of the *T. delbrueckii* IGC5321 strain showed intrinsic osmotolerance and ion toxicity resistance (Hernández-López and others 2003). Quite remarkably, stress signaling pathways, like the HOG or the calcineurin-Crz1p pathways, seem to have evolved in this non-conventional yeast in a niche-dependent way, which may explain the high resistance to Na^+ stress in this species (Hernández-López and others 2006a, 2006b).

The demand by the baking industry for new products with better or more sophisticated properties make the search of non-*Saccharomyces* yeasts an interesting and promising task. There must be a clear incentive, however, especially for processes and products with higher commercial value to overcome the natural resistance of yeast producers and consumers to technological changes.

Acknowledgments

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9
Other Leavening Agents

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Introduction

The production of carbon dioxide is responsible for the fermentation/expansion of a dough or batter and is important for the crumb structure. The crumb structure is the result of a certain "lightness", which is important for the properties of a baked good such as volume, shape, flavor development, tenderness, and brittleness,

Carbon dioxide is produced by yeast, microorganisms (sourdough), and chemical leavenings. Each leavening agent has specific characteristics that makes it suitable for the application in some products. Each leavening agent also has his limitations.

Carbon dioxide is the most important factor for leavening, but other gases (ammonia gas), water as steam, and incorporated air (introduced during the mixing process) also play a role in the expansion of baked goods.

Chemical leavening

Chemical leaveners are a group of leavening agents, mostly inorganic salts that react to produce gases when added to dough either singly or in combination (Manley 2000).

Carbon dioxide is the main leavening gas and is produced by either decomposition, where ammonium bicarbonate produces ammonia, water, and carbon dioxide, in the presence of water, or by the reaction of an acidic salt and sodium bicarbonate in the presence of moisture and heat to form a salt, water, and carbon dioxide (= chemical neutralization) (Holmes and Hoseney 1987).

Decomposition

Decomposition is dependent on the breakdown of the leavening agent in the presence of moisture or heat. A classical example of decomposition is ammonium bicarbonate. At a dough temperature of 59 °C, ammonium bicarbonate decomposes into ammonia gas, water, and carbon dioxide. All these by-products can provide leavening gases that can expand during the baking process (Heidolph 1996).

Chemical neutralization

Chemical neutralization is the process where a bicarbonate is neutralized by an acid. When a batter is prepared (in the liquid phase), sodium bicarbonate quickly solubilizes and is ready to react with the acid salt. The source of acidity can be a traditional leavening acid or acidity from other components in the formulation. The rate at which carbon dioxide is released is associated with the rate at which the proton from the acid becomes available to react with the bicarbonate. Each leavening acid has its own timing of release and rate of reaction. Some components in the dough or batter formulation can affect the reaction rate.

During chemical neutralization, carbon dioxide is the primary source of leavening. Water can eventually form steam. The neutral salt formed will have an impact on the final baked product: characteristics such as flavor, odor, color, crumb, and moisture are affected (Heidolph 1996). Discoloration and alkaline taste can result from thermal degradation of sodium bicarbonate, when not completely neutralized (Bennion and Bamford 1997). Organic acids can give their own flavor, ammonium salts can produce a specific odor in the baked product, when not completely volatilized out of the product (Heidolph 1996).

Aspects in formulating chemical leaveners

Chemical leaveners are commonly known as "baking powders" and are incorporated in products such as cakes and cookies. The two commonly used parameters for the formulation and evaluation of baking powders are neutralization value and dough rate of reaction. It is important that a correct ratio of acid and base is calculated since a neutral pH has to be reached. If not, it may affect color, taste, and crumb texture of the baked goods (Ali and Hasnain 2011).

Neutralizing value

The concept of neutralizing value (NV) was developed to compare the available acidity (CO_2-releasing power) of various leaveners and to calculate the correct level of usage. NV is defined as the parts by weight of sodium bicarbonate that will neutralize 100 parts by weight of an acid leavener so as to convert the bicarbonate to carbon dioxide (Holmes and Hoseney 1987).The NV indicates how much acid is needed in combination with a certain quantity of sodium bicarbonate.

Leavening acids are characterized by a specified minimum NV (normally when used with sodium bicarbonate). Used with other bicarbonates, the NV changes. The NV and the quantity of acid can easily be calculated (Figure 9.1). The leavening acid and sodium bicarbonate are used in such amounts that, after a baking process, none or only small amounts of residual acid or soda are left in the end product.

$$NV = (g\ NaHCO_3 * 100)/g\ acid\ and\ g\ acid = (g\ NaHCO_3 * 100)/NV$$

Figure 9.1 Calculation of neutralizing value and amount of leavening acid.

Dough rate of reaction

For chemically leavened products, the dough rise takes place in different steps, starting during the mixing step and ending in the oven. Two kinds of reaction rates are important: the direct reaction at room temperature (dough rate of reaction) and the reaction during the baking process (batter rate of reaction); both depend on the solubility of the acid.

The dough rate of reaction is used as a guide because it gives information about the reaction rates for leavening acids under controlled conditions. Increase in temperature, mixing time or addition of some ingredients can affect the rate of reaction. Higher temperatures and moisture levels accelerate the rate of reaction. Sugar, which competes for the water, suppresses the rate of reaction (Heidolph 1996). Fats and sugars have a delaying effect on the action of chemical leaveners (Chevallier and others 2000).

Leavening agents

Chemical leaveners or baking powders are divided into three groups, based on the type of gas producing component: sodium bicarbonate, potassium bicarbonate, and ammonium bicarbonate.

Sodium bicarbonate

Sodium bicarbonate, or baking soda ($NaHCO_3$), decomposes under the influence of heat into sodium carbonate, water, and carbon dioxide. Carbon dioxide is less soluble in water, and escapes as a gas. In an acidic environment, sodium carbonate (Na_2CO_3) also decomposes with the formation of carbon dioxide.

The use of sodium bicarbonate has some disadvantages. Not more than approximately 25% of the sodium bicarbonate dissolves and the residue as well as the sodium carbonate create an alkaline environment which causes chemical deterioration. This chemical decay expresses itself in a yellowish crumb and surface coloration with an unpleasant taste, especially at a higher dose (Manley 2000).

In a moist environment and in the presence of an acid, decomposition of sodium bicarbonate already takes place partially at room temperature. At the end, decomposition is almost complete and a sodium salt is formed instead of sodium carbonate. The choice of the acid determines the rate of reaction and thus the baking behavior.

Sodium bicarbonate exists in a variety of granulations. Granulation does not significantly affect the overall rate of release of carbon dioxide, but will influence the rate of solubility of the sodium bicarbonate. If granulation is too large, brown spots can be observed on the surface of the baked product due to poor dissolution, resulting in areas of localized alkalinity. High pH favors the Maillard reactions, which take place later in the baking process during the browning phase (Heidolph 1996).

Potassium bicarbonate

Like sodium bicarbonate, potassium bicarbonate ($KHCO_3$) decomposes under the influence of heat, thus releasing carbon dioxide. For a complete decomposition, an acid and a long baking process are required. Due to the slow decomposition, a clear spread and fine crumb structure are noticed. When decomposition is not complete, discoloration and a bitter flavor are present. Potassium bicarbonate is often used when the amount of sodium has to be reduced.

Ammonium bicarbonate

Ammonium bicarbonate (NH_4HCO_3) decomposes very rapidly at temperatures above about 60 °C. This decomposition releases ammonia gas (NH_3), water, and carbon dioxide. Ammonia as well as carbon dioxide escape as gases, so no residues are left in the baked product. When the formula contains a high moisture level, however, ammonia will dissolve in the water phase and affect the flavor.

Ammonium bicarbonate is often used in biscuit manufacture, where the low finished moisture content ensures minimal retention of dissolved ammonia. Since ammonium bicarbonate decomposes very fast during heating, it has a rising effect, and less spread, which results in a coarse structure, and a big volume.

Acidulants and acids

Baking powder is a mixture of sodium bicarbonate and either an acid or a salt that dissociates to give an acidic reaction in solution. The purpose of this combination of chemicals is to produce bubbles of carbon dioxide gas either before baking or, more particularly, as the dough is heated in the oven. These gas bubbles form the nucleation sites for further expansion as the gas is heated and the vapor pressure of water rises during the baking. It is therefore important that many, very small bubbles are present to produce a fine, even texture in the baked product (Manley 2000).

Almost every acid can be used for the dissociation reaction, but in practice a small group is applied. The original acidulants were soured milk (lactic acid) and cream of tartar (potassium acid tartrate). Lactic acid reacts fast, as early as the the mixing stage, and affects the flavor of the baked product. Nowadays technology has developed to use other compounds which are cheaper and less readily reactive so that the carbon dioxide is liberated during the baking stages rather than in the mixer. The use of acidic salts offers further possibilities to regulate the leavening activity. Acidic salts are complex acids, that are partially neutralized, or other complex salts, that react as acids. These salts are mixed, in advance, with sodium bicarbonate in the correct ratio. Starch or flour can be added to this mixture to separate the alkaline component from the acidic component and to bind water. This is a so-called baking powder.

The acidulants and acids have to be adapted in nature and concentration so that: (1) a controlled quantity of carbon dioxide is released, (2) the rate is controlled, (3) and no unreacted acidulant or bicarbonate is left at the end of the reaction. These acidic products are: (1) fast acting (products that dissolve quickly at low temperatures in water), (2) slow acting (products that dissolve when the temperature increases and only then release carbon dioxide), (3) mixtures of fast acting and slow acting products (most carbon dioxide is released between 45 and 70 °C).

Monocalcium phosphate monohydrate

Monocalcium phosphate monohydrate ($\mathbf{Ca(H_2PO_4)_2 \cdot H_2O}$) is a nucleating leavening acid and reacts quickly, typically during mixing. This product is available in several particle sizes. It is necessary to use a finely powdered form to reduce the possibility of black specks on the surface of baked goods.

Anhydrous monocalcium phosphate

Anhydrous monocalcium phosphate ($\mathbf{Ca(H_2PO_4)_2}$) has a phosphate-based coating that delays the leavening action by slowing its dissolution. This coating provides stabilization of the leavening system during storage of a dry mix (Heidolph 1996). The reaction with sodium bicarbonate is expressed by :

$$3\,Ca(H_2PO_4)_2 + 8\,NaHCO_3 \rightarrow Ca_3(PO4)_2$$
$$+\,4\,Na_2HPO_4 + 8\,CO_2 + 8\,H_2O$$

<div align="right">(9.1)</div>
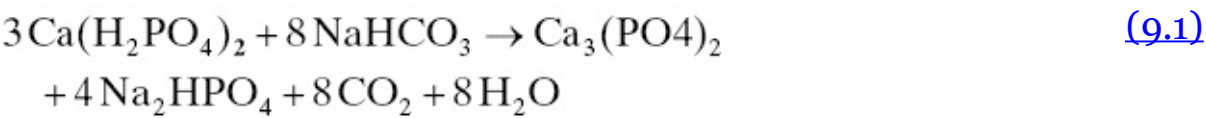
Sodium acid pyrophosphate

Sodium acid pyrophosphate (SAPP) is widely used and manufactured in several grades, in order of their increasing rate of reaction: 21, 26, 28, 37, 40, 43, and 45. The medium grade (SAPP 28) is commonly used, but a slow release grade is very suitable for use in a continuous sponge batter production since it minimizes the change in batter-relative density during standing. Solid SAPP is stable, not hygroscopic and hardly soluble in cold water. It is readily soluble in hot water, it is slow acting with sodium bicarbonate and reacts mostly in the oven according to Equation 9.2:

$$Na_2H_2P_2O_7 + 2\,NaHCO_3 \rightarrow Na_4P_2O_7 \\ + 2\,CO_2 + 2\,H_2O \tag{9.2}$$
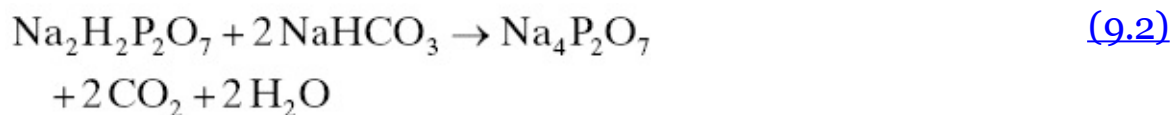
Sodium aluminium phosphate

Sodium aluminium phosphate (SALP or $\mathbf{NaH_{14}Al_3(PO_4)_8 \cdot 4H_2O}$) is a slow-release acid which has no after-taste. Its major leavening action takes place when heated. The benefits of using SALP are: consistency in leavening rate throughout dough and batter storage and use; increased crumb whiteness; and maintained batter thickness and consistency. SALP leavening acids contribute to uniformity in shape and texture and provide a neutral flavor (Heidolph 1996).

Sodium aluminium sulfate

Sodium aluminium sulfate ($\mathbf{Al_2(SO_4)_3 \cdot Na_2SO_4}$) is slow acting and releases carbon dioxide when heated. The rate of release is too slow to give maximum spring in the oven. It is mostly combined with monocalcium phosphate monohydrate to provide early expansion in baking. The flavor of sodium aluminium sulfate is a concern in some applications.

Cream of tartar

Cream of tartar or potassium bitartrate, $\mathbf{KHC_4H_4O_6}$, is slightly soluble in cold water. There is little reaction in combination with sodium bicarbonate, but the releasing rate is much faster when heated in the oven. Carbon dioxide is released according Equation 9.3:

$$KHC_4H_4O_6 + NaHCO_3 \rightarrow CO_2 \\ + KNaC_4H_4O_6 + H_2O \tag{9.3}$$
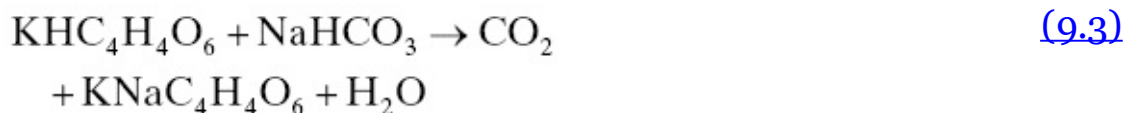
Tartaric acid

Tartaric acid is fast acting and soluble in both cold and hot water. It reacts immediately in combination with sodium bicarbonate (Equation 9.4):

$$H_2C_4H_4O_6 + 2\,NaHCO_3 \rightarrow 2\,CO_2$$
$$+ Na_2C_4H_4O_6 + 2\,H_2O$$
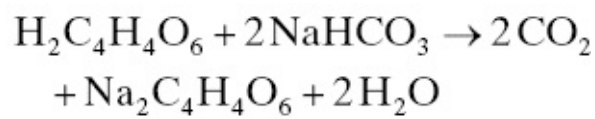
Sodium tartrate, the residual salt, has a laxative action. Some people do not prefer the use of tartrates in the baking industry. In practice, no problems with the use of tartrates are reported, because the quantities added are very small.

Glucono-delta-lactone

Glucono-delta-lactone ($C_6O_6H_{10}$) is a slow-releasing leavening agent which produces carbon dioxide continuously. It is an intramolecular ester of gluconic acid with an initial sweet taste but a slightly acidic after-taste. Ambient temperature gives a slow hydrolysis, higher temperatures give faster hydrolysis times (Bennion and others 1997). Glucono-delta-lactone can also be used in bread making, as a replacement for yeast, because of the slow constant release.

Role of leavening agents

Leavening agents play various roles in baked products. The capability of leavening agents to give baked products a high volume and aerated structure is the most important activity, but not the only one.

Effect on baked product grain

Leavening agents affect the grain of baked products. Cell wall thickness, cell size, shape, and uniformity determine the grain. Incorporated air, originated from the mixing step, and leavening gas affect the grain. An ideal situation (with many small gas cells) creates a fine, uniform grain in the baked product. Therefore time, temperature, ingredients, formulation, and mixing have to be optimal (Vetter and Zeak 1989).

Effect on baked product texture

Texture can be described as the hardness or tenderness of a product. Mostly, there is a relationship between grain and texture. An open grain will result in a softer texture, a dense grain will give smaller volumes and so a more hard texture. Also the recipe has an influence on texture. Higher amounts of shortening, less sugar or a softer flour result in softer products. Recipes with high levels of shortening and sugar require lower levels of leavening to reach a desired volume and softness. Hard products can become softer by using higher levels of leavening (Vetter and Zeak 1989).

Effect on spread

For cookies, some spread is always noticed during baking. Spread is an important characteristic, not only for the end product quality, but also for packaging (dimensions of the baked product). Therefore it is important that spread is kept under control. Variations due to flour quality, baking conditions, recipe formulation, and so on, can occur. Spread can be controlled by a number of options – such as flour quality, sugar level, shortening level – including adjustment in leavening (Vetter and Zeak 1989).

Effect on height

Most cookies do not rise very much during baking, in contrast to other products such as cakes. In cakes, chemical leaveners have an effect on volume, crumb grain, and crumb structure, crumb softness, and so on.

Effect on surface cracks

In cookie making, surface cracks can occur and are not desired. Since leavening has an effect on the spread, it also effects the surface. Surface cracks are formed when leavening gas is released from a still molten internal dough after the top exterior surface of the cookies has been set by the heat of baking. Therefore, a delayed release of gas from the leavener will result in surface cracks. Surface cracks can be eliminated by delaying the setting of the

surface dough or by a faster gas release (Vetter and Zeak 1989).

Effect on color and flavor

Appearance and color play an important role in consumer product acceptance. Leavening agents influence product color by their effect on the pH. An alkaline pH accelerates browning, an acidic pH retards browning. A leavener influences the pH by the alkaline action of the carbon dioxide producer (soda). The pH can be neutralized by adding more acidic components or by augmenting the acidity. A properly balanced leavening system is one in which the quantities of leavening acids are just enough to offset the alkalinity of the soda, resulting in a finished product pH close to neutral (Vetter and Zeak 1989).

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10
Ascorbic Acid and Redox Agents in Bakery Systems

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Introduction

Oxidizing and reducing (redox) agents are highly active materials which are widely used in the baking industry to modify the physical properties of dough and batter systems. These include chemical-based materials such as ascorbic acid, azodicarbonamide, and potassium bromate as oxidizing agents and sodium metabisulfite and L-cysteine as reducing agents. In addition to these chemical-based redox materials, a whole range of enzymes are being used to modify dough behavior. Examples include glucose oxidase and sulfhydral oxidase that are typically used in combination with ascorbic acid, all requiring the presence of oxygen to function effectively. Other important enzymes are proteases that soften and transglutaminase that strengthens dough systems by cross-linking protein chains.

There are many reasons for using materials that change dough physical properties. One reason is that flour properties can vary widely in baking performance and this causes considerable problems in plant bakeries that are geared to large-scale production. Redox agents can help flours to perform in a more uniform way so that the performance is more consistent from one day to the next. The processing of different bakery products also requires a range of dough characteristics. Bread dough, for example, requires a good balance of viscoelastic properties that possess good gas-holding properties, whereas biscuit dough should possess plastic behavior for good sheeting properties. The baking processes being used have also had an impact on the redox agents being used. The development of new, fast bread making processes has meant that the time required to convert raw materials into baked bread has been reduced from about 5 h to around 2 h. In addition, the craft skills needed to control dough properties has been replaced by precise control of dough mixing and this has placed a greater reliance on the use of redox agents. This chapter reviews some of the commonly used chemical redox agents, but focuses particularly on selected enzymes that influence dough properties by drawing on work carried out at Campden BRI.

Basics of dough development

Proteins consist of sequences of amino acids joined together to form chains called polypeptides. The peptides can exist as random shapes or fold in a particular way to form regular shapes such as helices. A number of chains can also associate to form aggregates and hence large complex structures. The folding of polypeptide chains results from chemical bonds and the combination of weaker hydrophobic or H-bonds between amino acids. These bonds can also hold large aggregates together. The important bond for protein cross-linking is without doubt the disulfide bond (SS) formed between amino acids containing sulfhydryl groups (SH). In basic terms, the SH groups represent the free or the reduced form of the proteins and in this condition the protein polypeptides exist as individual free chains. When oxidized, however, two SH groups become joined together and form a SS bond, and as proteins can possess a number of amino acids that contain SH groups, a chain can be linked together to several other chains and form an extensive network that determines the rheological properties of dough systems. This is one mechanism by which gluten development and the action of redox materials is typically explained.

In flour, the important proteins that are thought to be involved in the formation of viscoelastic structures are the glutenins and gliadins. Both classes of proteins are important for creating a gluten network capable of holding gas and expanding. Gliadins are responsible for the viscosity and the extensibility of the dough. Although gliadins contain a number of cysteine amino acids, they only form intramolecular SS bonds, hence they are not involved in the network structure of gluten (Weiser 2007). Glutenins contain an additional cysteine compared with gliadins and this is located at the end of the chain so that it is in a prime position to form SS bonds with other glutenin proteins and contribute to the gluten network formation (Wieser 2007). The links formed by SS and other types of bonds can be broken chemically or by physical methods such as the shearing forces during dough mixing. These can cause a large change in the characteristic property of the protein chain and, once deprived of the SS bond, it can unravel and hence interact with different chains. It is at this stage that the action of oxidizing materials is thought to be important, forming new cross-links during mixing, proofing, and baking. The oxidation action and the formation of SS bonds linking protein chains together is the key basis in the formation of the viscoelastic structure of gluten.

Redox requirements in different bread making processes

The bread making process relies heavily on the function of redox agents, with different bread making methods placing different demands on the levels of these materials. The traditional long fermentation processes required small amounts of material (5–20 ppm on flour weight) to control the uniformity of the bread produced. The faster processes such as the Chorleywood Bread Process (CBP) typically use levels of 60–100 ppm on flour weight, although higher levels are not unusual. Continuous processes require high levels of oxidation similar to those of the fast or no-time dough processes. The development of the Activated Dough Development (ADD) method also brought another significant change in the bread making industry by introducing the reducing agent L-cysteine hydrochloride. This was an interesting process in which the use of L-cysteine permitted the elimination of bulk fermentation, but without the intense use of mechanical development. The rapid development of dough by ADD was in fact brought about by the combined effects of oxidizing and reducing agents. The resulting action produced soft and pliable dough. By itself, L-cysteine created low volume and poor crumb structure, probably due to excessive depolymerization of the gluten-forming proteins by the reducing action on the disulfide bonds. However, in the presence of an oxidizing agent such as ascorbic acid, the use of L-cysteine produced bread with a bigger volume and a finer crumb structure.

Ascorbic acid

Ascorbic acid is widely used by the baking industry and in some countries, for example in the United Kingdom, is the sole chemical oxidizing agent used in the manufacturing of bread and other baked goods. It is a naturally occurring material found in fruits and vegetables and is commonly known as vitamin C. However, most of the ascorbic acid used in food processing and production is synthesized from glucose using a combination of fermentation and chemical methods. Ascorbic acid itself is a reducing agent but in the presence of oxygen gas and an enzyme – ascorbic acid oxidase which is naturally found in wheat flour – the ascorbic acid is converted to the dehydro form as shown in Figure 10.1. It is this form which has the potential to take part in oxidation reactions such as the SH/SS interchange and to help stabilize the gluten protein network. The use of ascorbic acid in bread making leads to greater loaf volume and a finer more uniform crumb structure. This can only occur as long as oxygen is present to convert the ascorbic acid into its oxidizing form. The action of ascorbic is largely complete soon after the end of mixing, at which stage in the process yeast and other chemical reactions compete for the available oxygen.
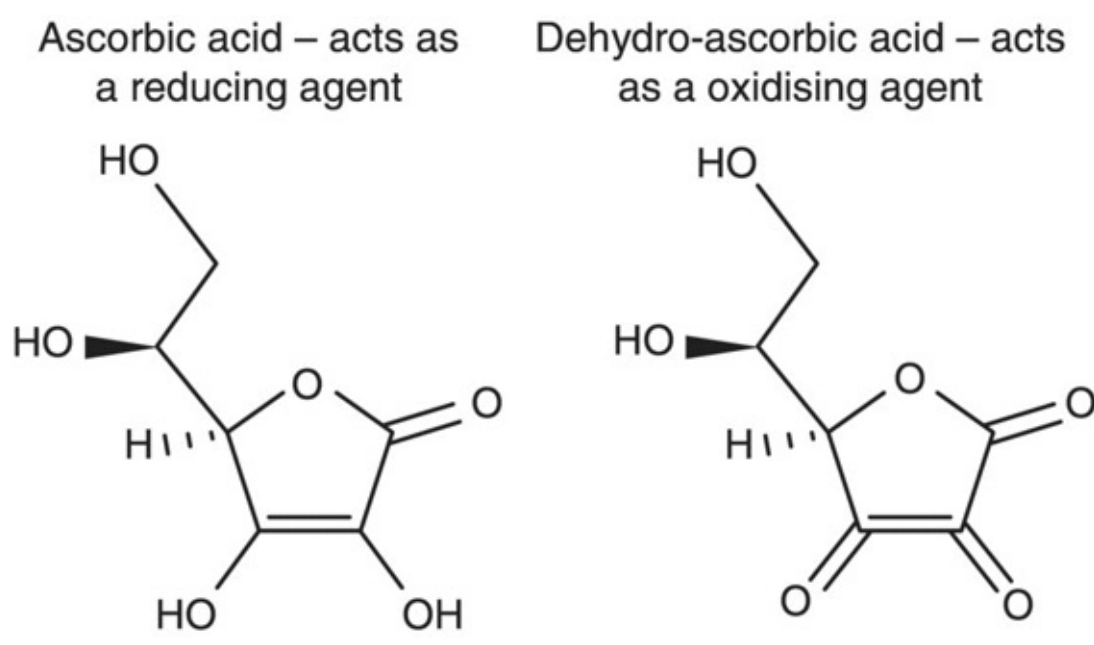
Figure 10.1 Chemical formulae of ascorbic acid and dehydro-ascorbic acid.

The SH/SS interchange reaction between neighboring protein chains containing SH groups is thought to be an important mechanism in gluten network development. Another possible reaction of this type is thought to involve glutathione, which occurs naturally in flour, but is thought to affect gluten network formation by undergoing SH/SS interchange reactions with protein chains. If this is not prevented, the number of cross-links formed in the gluten network decreases and weaker more extensible gluten is produced. The enzyme glutathione oxidase plays a role in gluten stabilization by preventing this happening. It does this by forming glutathione dimers, thus blocking the pathway that leads to gluten depolymerization (Grosch and Weiser 1999).

As mentioned earlier, some plants and fruits can possess elevated levels of ascorbic acid and this presents an opportunity to use these to provide the ascorbic requirement in bakery products. This has an advantage in that the chemically synthesized version has an E-number

and must be declared on the label as ascorbic acid, vitamin C or E300. Examples of materials with ascorbic acid activity include acerola cherry and kakadu plum containing 15–20 mg/g of material ascorbic acid. The performance of acerola cherry was evaluated in Farinograph mixing trials and compared with a chemically synthesized commercial sample. Evidence in Figure 10.2 shows that both forms of ascorbic acid worked equally well during dough development. In fact, baking trials suggested that an amount of acerola powder that contained a lower level of ascorbic acid could be used to give a similar performance to the commercial version. This may be due to the natural material containing additional antioxidant materials that also take part in oxidation reactions in dough and hence support the oxidizing activity of the ascorbic acid.
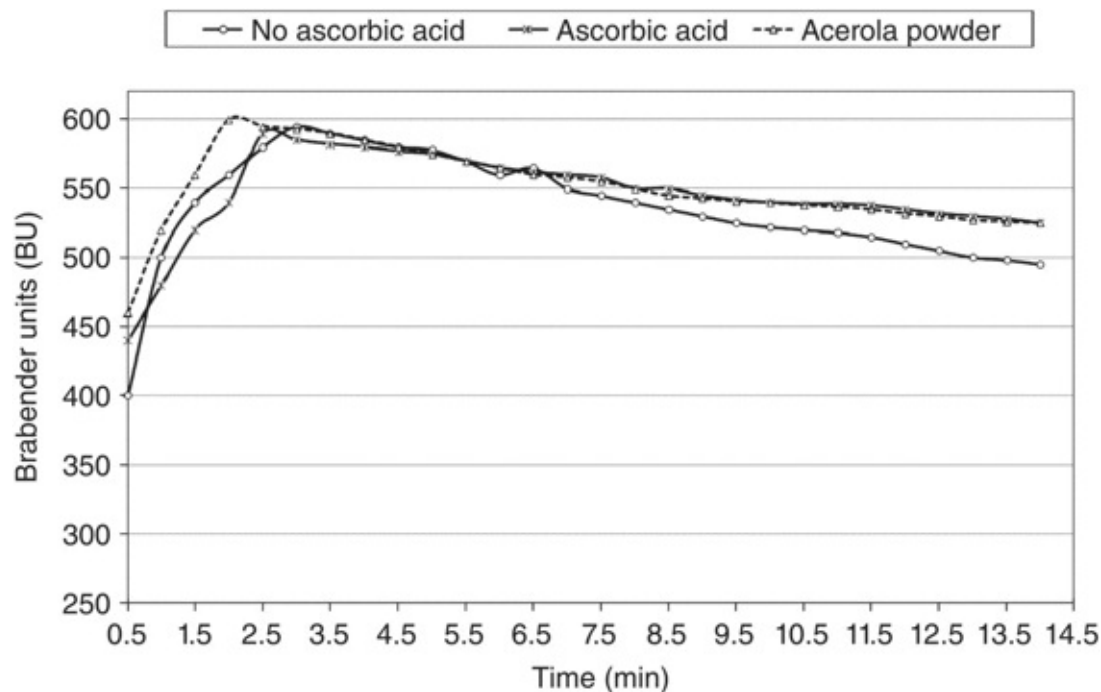
Figure 10.2 Mixing performance of acerola cherry powder compared with chemically synthesized ascorbic acid. Courtesy of Campden BRI.

Naturally present antioxidant materials such as polyphenols are one example of materials that may also react in dough systems and modify dough properties. If the action of such materials was proved to be additive then it may be possible to use natural materials to deliver a lower concentration of ascorbic acid in a recipe and rely on the activity of other materials to provide additional oxidation to make up for the lower amount of ascorbate. This is an area of research that has not been fully explored.

Oxygen

Air incorporated into the dough during mixing contains 20% oxygen, which is reported to affect gluten cross-linking (Xu 2001). The importance of oxygen in dough development was appreciated by Tsen and Bushuk (1963), who observed that when dough was mixed in oxygen it was more resistant and less extensible compared with dough mixed in a nitrogen atmosphere. Early work at the Flour Milling and Baking Research Association (Chorleywood, Hertfordshire, UK) also found that dough processed through a laboratory-scale continuous mixer using a pressurized feed chamber, produced bread that exhibited characteristics of increased oxidation compared with the same dough at atmospheric pressure. The belief was that the result may have been due to greater oxidation from the oxygen in the air trapped in the dough bubble structure during mixing with forced air under compression. Incidentally, bread made with 100% oxygen had a similar structure to that made when mixing dough in a high vacuum as reported by Baker and Mize (1941). It was soon realized that yeast activity in the dough removed oxygen rapidly from the dough and if the only gas was oxygen the bubble structure disappeared. Further investigations indicated that a mixture of 60% oxygen/40% nitrogen in combination with ascorbic acid provided a dough of a similar density to that mixed in a partial vacuum and furthermore it provided an oxidizing improvement and a bleaching effect to give a white crumb with a fine and uniform structure. Work reported by Xu (2001) also stated that the effects of oxygen were concentration dependent and that oxygen was depleted from a mixer atmosphere even in un-yeasted doughs. Even now it is still unclear what the exact mechanism of oxygen action is in the dough.

Azodicarbonamide

Azodicarbonamide (ADA) is a fast acting oxidizing agent. Its action oxidizes free SH groups in flour proteins and strengthens dough. This action is particularly effective in modifying the dough properties of poor-quality flours by improving the processing behavior and gas retention properties (Joiner and others 1963). The same researchers also reported that ADA used at the correct level gave increased bread volume and good crumb properties, but overdosing depressed loaf volume. Its fast reaction rate can be a problem in some bread making methods, but not so in the CBP where the short mixing time matches the reaction time of the improver.

Use of ADA is banned in EU countries, but is still used in others. The key reason for the ban is the presence of a reaction product, semicarbazide, which is present in breadcrumb and crust (Noonan and others 2008) and poses a health risk.

Potassium bromate

Potassium bromate, commonly known as bromate in the industry, has been used widely in the baking industry, but health concerns have led to bans in the EU and other countries, although it is still in use in the United States. Bromate acts on the gluten forming proteins in flour where it increases dough strength producing bread with good volume and fine uniform crumb structure. It is considered to be slow acting in comparison with other oxidizing agents, with little impact observed during the mixing stage. Bromate functions largely in the more lengthy proving and into the early stages of baking. The reason for this is that the rate of reaction of bromate is temperature dependent, with the rate increasing as the temperature is raised, and this is what happens in practice as the dough is mixed, proved, and baked. It has a powerful action and so inaccurate usage can lead to over-oxidation of dough.

It has been usual practice to use bromate in combination with ascorbic acid to enhance its effectiveness. Ascorbic acid requires oxygen, which diminishes quite quickly, and it is likely that the action of ascorbic acid is less important after mixing. This is where bromate is thought to become active and provide the oxidation activity that is required in the dough due to continued cross-linking of the gluten matrix by facilitating SH/SS exchange reactions. There is also expected to be an additional demand for redox activity as a consequence of yeast metabolism generating small sulfhydral compounds that could potentially weaken the gluten matrix, again by SH/SS interchange reactions. The release of small sulfhydral compounds would be expected to continue up to the stage where yeast activity ceases at about 55 °C during baking; hence the continued supply of oxidation capacity is essential to maintain the strength and integrity of the gluten matrix.

L-Cysteine hydrochloride

L-Cysteine is a naturally occurring amino acid that has the functional feature of a free SH group in the molecule. This group allows the L-cysteine to break disulfide bonds between gluten-forming proteins by SH/SS interchange reactions thus decreasing the number of cross-links between aggregated proteins. The resulting dough is softer with lower viscoelastic properties and greater extensibility. The dough produced is reported to be more cohesive with improved machinability (Angioloni and Rosa 2007). The mechanism of action of L-cysteine is similar to that of glutathione, as are the changes observed in the dough properties. L-Cysteine plays a key role in the ADD process where it helps to break disulfide bonds between gluten forming proteins in the same way as high shear mixing processes use mechanical energy to break bonds. L-Cysteine used alone would not be beneficial to a dough system, as the end result would be production of L-cysteine–glutenin complexes with little potential for extensive cross-link formation. Such doughs would possess an imbalance in the viscoelastic properties and lack suitable properties for gas retention. This would result in bread with low volume and coarse crumb structure. L-Cysteine action however is used in the production of morning goods such as buns where a softer dough flows more when molded, avoiding the build-up of stress and hence quality defects in the final product.

L-Cysteine was investigated by Pecivova and others (2010) in combination with mixtures of reducing and oxidizing agents in the production of buns, and it was reported that the wheat flour dough had lower tenacity and higher extensibility. It was concluded that the cocktail of redox materials used, including L-cysteine, had a positive effect on bun quality.

Sodium metabisulfite

Sodium metabisulfite has been used in the processing of biscuit and pastry products because of its action as a gluten-softening agent. It helps to produce softer more extensible dough which has little or no recovery in thickness after sheeting. It has also found application in bread production in some countries where strong protein flours are worked with slow speed mixers requiring long mixing times. Sodium metabisulfite helps to decrease mixing time by breaking some of the covalent SS bonds holding the glutenin chains together, thus replacing in part the need for mechanical force to fully develop such doughs.

Research by Hlynka 1949 described the action of sodium metabisulfite on wheat gluten as a result of cleavage of disulfide bonds between protein chains. The chemistry of this reaction involves the hydrolysis of metabisulfite to bisulfite which then forms an equilibrium mixture with sulfite ions. It is the sulfite ions that cleave the disulfide bond resulting in a free sulfhydral group on a protein chain (Fitchett and Frazier 1985).

Sulfhydral oxidase

Sulfhydral oxidases catalyze the oxidation of SH groups in both small molecular weight compounds and in cysteine incorporated in protein chains. The reaction occurs in the presence of oxygen, which itself becomes reduced to hydrogen peroxide. It was reported that the effect of this enzyme was dependent on the source, with no effect measured with the same enzyme isolated from milk (Kaufman and Fennema 1987). Positive effects were measured with the fungal sulfhydral oxidase, however, especially when used together with glucose oxidase or hemicellulase (Souppe 2000). A more recent study investigated sulfhydral oxidase in combination with ascorbic acid in fresh and frozen dough systems (Faccio and others 2012). Use of the enzyme alone in an additive-free recipe resulted in a weaker more extensible dough while opposite effects were observed in the presence of ascorbic acid. The strengthening effect of the dough was dependent on the concentration of the enzyme and not on the amount of ascorbic acid. The strengthening mechanism on the dough by sulfhydral oxidase was postulated to be similar to that of ascorbic acid, which is by removal of reduced glutathione, thus positively affecting the ascorbate system (Faccio and others 2012). An alternative explanation was that the hydrogen peroxide produced by the reaction of the enzyme was directly able to convert ascorbic acid to its active form in the dough, namely dehydroascorbic acid.

Glucose oxidase

Glucose oxidase (GOX) is an interesting oxidizing enzyme which has found use in some commercial applications. The presence of endogenous activity of GOX has not been found (or detected) in wheat flour but its application in bread making, in combination with hemicelluases, has been patented (Haarasilta and others 1991). In the patent it was claimed that GOX in the presence of catalase and hemicellulases improved both the handling properties of the dough and the quality parameters of bread such as volume and texture. Like ascorbic acid, GOX requires the presence of oxygen to catalyze the oxidation of β-D-glucose to β-D-gluconolactone and in doing so it produces hydrogen peroxide.

GOX from *Aspergillus niger* has optimum activity at pH 5.6 while the optimum range was cited as pH 6.5–7.5 by Rakotozafy and others (1999). β-D-Gluconolactone is then slowly hydrolyzed to gluconic acid by a non-enzymic process. The hydrogen peroxide produced is able to oxidize rheologically active SH groups to form disulfide bonds (Haarasilta and Pullinen 1992). This change in the SH and SS groups has been demonstrated by Poulson and Hostrup (1998) where the addition of GOX showed a decrease in the thiol content. This was presumed to have been caused by oxidation by the hydrogen peroxide produced during the reaction of the enzyme. The SS bonds increase the number of cross-links in the gluten network, strengthening the dough system, and enabling better gas retention in the dough (Wiksrom and Eliasson 1998; Vemulapalli and others 1998). These rheological changes in dough systems have also been investigated by the author whereby increasing addition of the GOX enzyme was shown to increase the elastic modulus of the dough (see Figure 10.3). However, it was also found that the loaf volume did not benefit from this change in the dough properties.
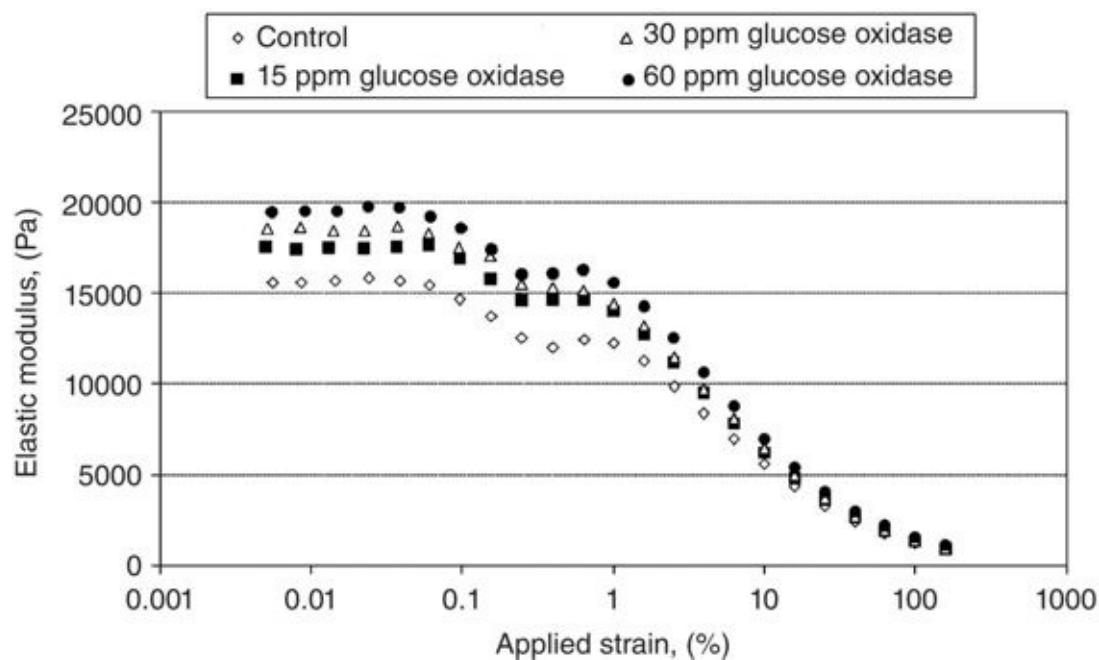
Figure 10.3 Effect of glucose oxidase on dough elastic modulus. Courtesy of Campden BRI.

Dough quality is a vital factor in delivering good loaf volume and crumb quality in the baked product. The hydrogen peroxide produced by the action of GOX may also take part in another important reaction that may help to improve the properties of the dough. It has been demonstrated that the addition of hydrogen peroxide to a flour suspension increased the

viscosity of the solution by gel formation (Izydorczyk and others 1990). This type of gelling induced by an oxidizing agent has been termed oxidative gelation and involves a pentosan fraction that contains ferulic acid (Moore and others 1990). Not all oxidizing agents are able to initiate gel formation, for example, ascorbic acid and potassium bromate are unable to do this, suggesting that the mechanism of gelation of these oxidizing agents differs from that of GOX (Hoseney and Faubion 1981). The gel formed during oxidation influences the viscoelastic behavior of the dough, and the elastic modulus of water-soluble (Izydorczyk and others 1990) and water-insoluble pentosans (Michniewicz and others 1990). Gel formation is thought to improve the gas retention properties of the dough and promote improvement in loaf volume.

Exogenous GOX has been shown to be susceptible to denaturation during dough development (Rakotozafy and others 1999). The process of mixing induced a decline in activity of the enzyme in supplemented doughs, to the extent that 25% of GOX activity was lost in the first 5 min of mixing and an additional 20% was lost after 20 min of mixing. A limitation to GOX activity is certainly the availability of oxygen in the mass of the dough, which is competitively required by yeast and other chemical reactions. This means that it is only the surface of the dough which is exposed to the atmosphere and is likely to benefit from GOX activity. This fact is exploited in commercial practice where hemicellulases are used to process doughs, a practice that can lead to doughs becoming too soft and sticky. This can cause handling problems on the plant where dough comes into contact with equipment surfaces. Inclusion of GOX causes drying of the dough surface and alleviates problems related to overdosing or increased processing time when using hydrolytic enzymes such as hemicellulases.

Studies carried out by the author also examined the possibility of using GOX to replace ascorbic acid. Bread made with GOX alone had a low volume and a coarse crumb texture (Figure 10.4b) compared with ascorbic acid (Figure 10.4a). It was concluded that the functionality of ascorbic acid cannot be replaced by supplementing dough with GOX alone. This is probably because the mechanism of action of the two materials is different. The action of the GOX enzyme involves the generation of free radicals, whereas ascorbic acid is first converted to dehydroascorbic acid which then takes part in SH/SS exchange reactions. When ascorbic acid is used as an improver in the CBP, the result depends on the mixing atmosphere, with the best results being obtained in an oxygen-enriched atmosphere with 60% oxygen and 40% nitrogen.

(a)

(b)

Figure 10.4 Effect of glucose oxidase on bread properties. Bread made with (a) a standard level of ascorbic acid and no glucose oxidase; (b) glucose oxidase and without ascorbic acid. (Courtesy of Campden BRI).

Transglutaminase (TG)

TG has been used for some years in the processing of meat, dairy, fish, and pharmaceutical products, but has only recently been investigated for use in bakery products (Kuraishi and others 2001). It occurs in animals but is produced on an industrial scale from microorganisms. The TG enzyme catalyzes acyl-transfer reactions, which introduce covalent cross-links between protein molecules. For example, cross-links are formed between lysine and glutamine residues without affecting the nutritional quality of the protein (Seguro and others 1996). This was thought to offer an alternative mechanism to the formation of cross-linkages by oxidation in wheat flour proteins in which the linkages would be more stable than cystine-disulfide bridges. The high molecular weight glutenin subunits are most affected by TG, while gliadins are affected to a lesser extent (Autio and others 2005). The enzyme itself is destroyed during baking and has been approved for use as a processing aid in food.

Experimental work in white pan bread was undertaken (Gerrard and others 1998; Poza 2002) to test the hypothesis that this enzyme might be beneficial in bread making. The results of these studies were positive in terms of, for example, strengthening of the crumb, increasing dough stability at higher dough moisture, while maintaining the same bread firmness levels. Evidence was produced that the enzyme formed cross-linkages and that the energy required to develop the dough could be decreased. The enzyme activity was not recorded and therefore it was difficult to compare the significance of the effects in a commercial process, or with material available in the United Kingdom. Other studies have formed the basis of patent claims (Gottmann and Spoessler 1994).

Investigations of TG in bread dough systems

Investigation of TG in model flour–water dough systems initially studied its effects during mixing by measuring the torque using a Do-corder. This was done while the dough developed at different enzyme concentrations. The results in Table 10.1 show that, with TG at 0.2% on flour weight, the mixing characteristics were similar to the control dough. However, at the 0.4% level, the mixing torque increased by more than 17% and reduced the mixing time by over 15% compared with the control. These changes (significant P 0.05) were indicative of an increase in cross-linking of the gluten polymer. These large molecules can form concatenations (Ewart 1979) in normal mechanical development via their sulfhydryl groups to form an elasticoviscous dough. The stronger the dough, the higher the torque value reaches in the development graph, and the results suggest that TG is forming additional cross-links to make the protein aggregates larger.

Table 10.1 Mixing characteristics of doughs with TG at different concentrations. Courtesy of Campden BRI.

TG concentration (%)	Mixing time (min)	Mixing torque (Nm)
0	3.20	1.50
0.2	3.25	1.55
0.4	2.80	1.75

The activity of TG was also studied using a 10% spray-dried wheat gluten dough with the enzyme added at different concentrations. The results at a concentration of 0.01% on gluten weight with strain sweep measurements of the elastic modulus carried out at different time intervals are given in Figure 10.5. There was a steady increase in the elastic modulus of 20–25% with time over 15 min compared with the modulus of the control dough. This indicated that the number of intermolecular interactions in the gluten material extending across the gel was increasing. The formation of covalent bonds by TG in proteins is usually between the glutaminyl residues and the amino groups of the lysine residues. There is a high content of glutamine and some lysine in wheat gluten protein, offering TG the opportunity to form cross-links. The elastic and viscous moduli of dough were influenced by TG to different degrees (Figure 10.6). After 15 min the elastic modulus had increased by 24%, but the viscous modulus had increased by only 11%. The ratio of viscous and elastic modulus (phase angle) decreased with time, indicating that the elastic properties of the dough were increasing at a faster rate than the viscous properties. In physical terms the system was becoming firmer and less fluid.
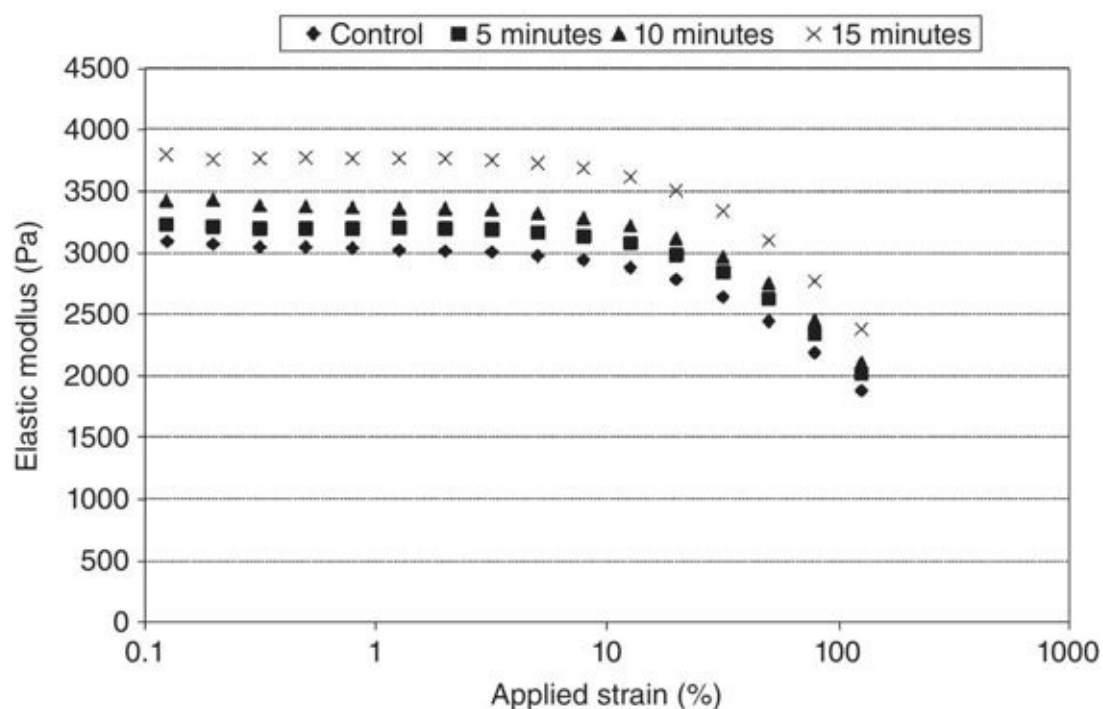
Figure 10.5 Effect of TG addition on the viscoelastic properties of hydrated gluten. Courtesy of Campden BRI.
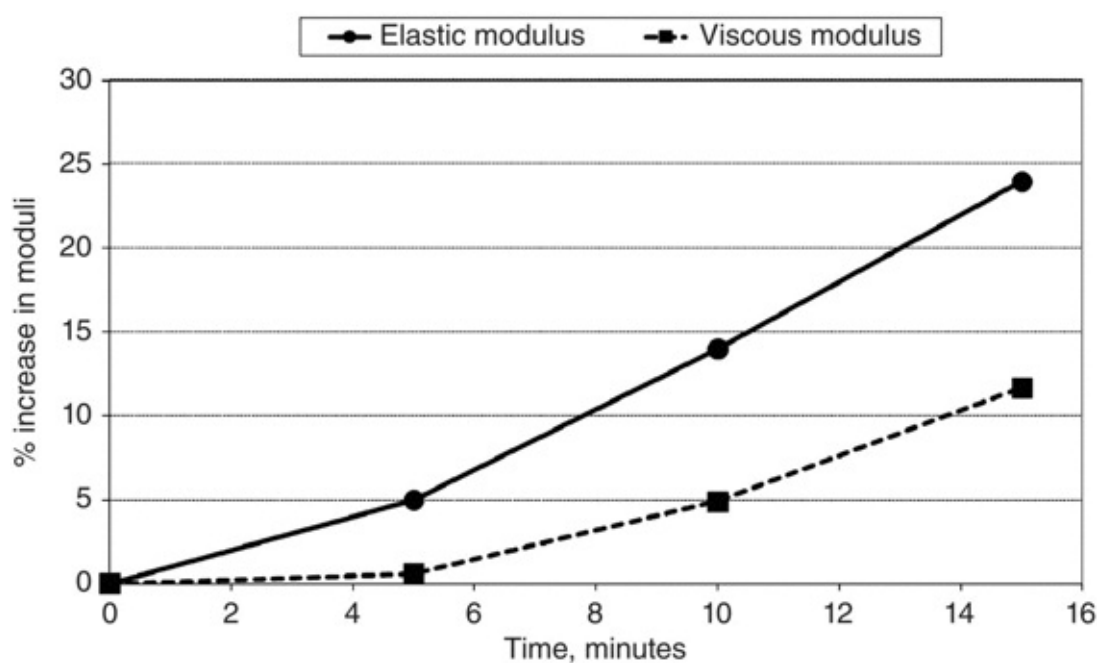
Figure 10.6 Effect of TG on the elastic and viscous moduli of gluten proteins with time. Courtesy of Campden BRI.

The study was then extended to a full bread recipe with dough developed using the CBP method. Dough properties were measured using small deformation oscillatory measurements with a rheometer. The results shown in Figure 10.7 reflect that for 40–60 min before baking, enzymes continued to react in the moist dough at 30–40 °C. In our study at 25 °C, the elastic modulus of control dough was found to fall during this period and became almost constant after 90 min. This change in dough rheology is probably caused by α- and β-amylases hydrolyzing damaged starch, reducing its average molecular size and releasing water to the gluten. Therefore, when TG is added to dough to act as a catalyst for cross-linking proteins, it must overcome the effects of hydrolytic enzymes by forming more solid structures in the continuous gluten phase. At the lowest level of addition for TG, there was an increase in elastic modulus for up to 30 min (see Figure 10.6) and then a continuous fall until the end of the test time. It might be concluded that initially the addition of the TG caused an increase in the dough elasticity by forming cross-linkages, but this increase was eventually counteracted and overtaken by the natural dough thinning process of the amylases, as observed in the control. However, further addition of TG showed a continuous increase in the elastic modulus for the full 90 min. This indicated that TG was increasing the number of cross-links in the protein phase to an even greater number and overcoming the thinning effect of the amylases.
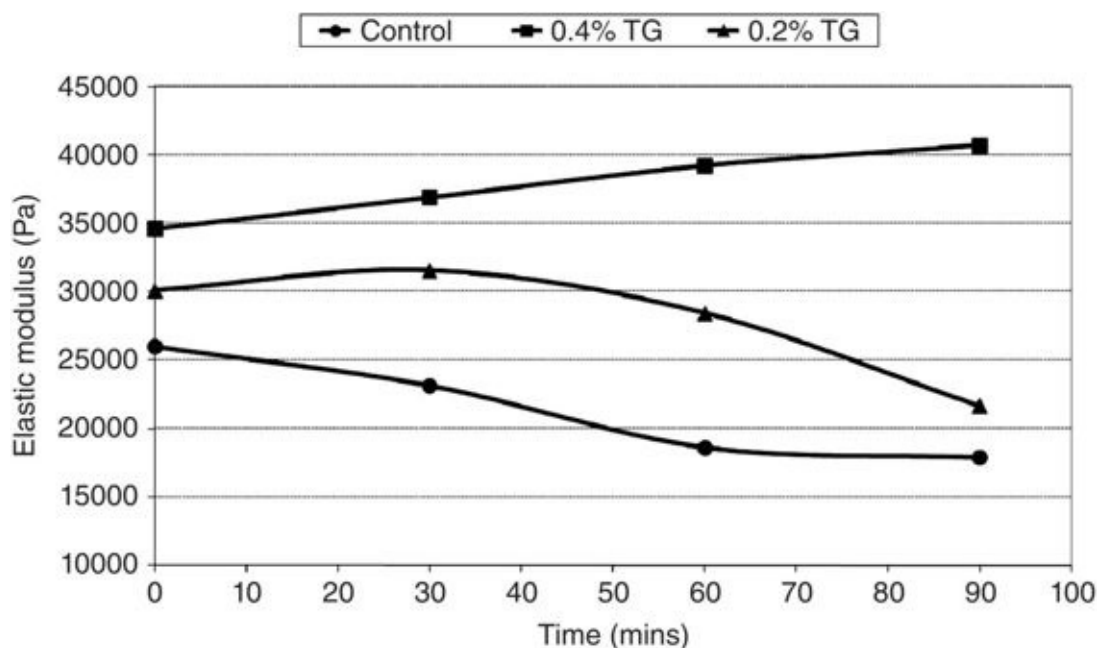
Figure 10.7 Effect of TG addition on dough elastic modulus. Courtesy of Campden BRI.

The doughs prepared for the rheological study were also used for studies of their protein characteristics. These were extracted in SDS and examined on PAGE with sets of standard proteins. There were some significant differences between the results for the proteins of the control dough with those of the TG doughs. The peaks with molecular weights from 74 to 120 kDa decreased with increasing TG. Some other peaks also decreased a little, but not as much as the high molecular weight peaks. At the same time, some very high molecular weight material appeared in the lanes of the TG doughs. This material is almost excluded from the gel and was estimated as being > 270 kDa. It did not appear in the proteins of the control dough. These results would suggest that proteins, from a range of molecular weights that contain the glutenins, are cross-linked by the TG and increase their molecular weight in new forms of covalently linked molecules. Other fractions were also cross-linked to a smaller degree.

Bread made with TG alone at 1000 ppm on flour weight showed reduced loaf volume by 5% compared with the control. TG restricted the expansion of the dough, as shown in Figure 10.8. However, it was found that when used in a combination with a xylanase, it helped to reduce dough stickiness while obtaining a 5% increase in loaf volume. These results suggested that there was a useful interaction between the two enzymes to provide a beneficial effect in bread.

(a)

Control bread

(b)

Bread made with 1000 ppm TG

Figure 10.8 Effect of TG addition on CBP bread quality. (Courtesy of Campden BRI).

Application of TG in puff pastry production

The ability to build up the protein structures in dough has also been applied to laminated pastries such as puff pastry and croissants (Gerrard 2003). It was found that a significant improvement in lift was obtained, resulting in larger products with lighter textures.

The effects of TG were also studied in puff pastry manufactured in the English style to produce vol-au-vent cases. At an enzyme level of 0.1% on flour weight there was a significant increase in baked height due to TG addition (Figure 10.9). There was an improvement in expansion of 5–10% in height for the lowest enzyme level (0.1%) but increased usage of enzyme showed in further increase. TG also had a stabilizing effect on the dough prior to baking. While the control dough lost a little height on standing an extra 15 min, the performance of the enzyme-treated dough remained the same.

Figure 10.9 Effect of TG addition on puff pastry height (from left to right: 0.3%, 0.1%, and 0% TG). Courtesy of Campden BRI.

Study of TG in wafer and cake batter systems

The effects of TG have been studied in more dilute systems compared with bread and pastry dough. In a wheat flour wafer batter of 30% solids, TG addition increased the viscosity of the batter over 10 min compared with a control batter. The increase in batter viscosity caused by TG addition was shown to increase with the concentration of enzyme added (Figure 10.10). Two cake flours, untreated and heat-treated, were examined in a model cake batter of 50% w/w solids with increasing levels of TG. The results in Figure 10.11 show that untreated flour is less viscous initially and responds slowly to TG addition, whereas the heat-treated flour is significantly more viscous and responds to a greater extent. Batter viscosity is beneficial to cake batter systems as it helps to slow down the diffusion of air bubbles out of the batter and into the atmosphere. Chlorinated flour was very useful in this respect as it was able to absorb more liquid in a batter system and produce a more viscous batter. In countries where chlorination of flour is banned, such as EU countries, this function in the flour has been replaced to an extent by heat treatment, with additional support achieved by gums and other materials. The action of TG in cross-linking proteins could be of practical importance in batters where the changes to the viscoelastic properties may help to stabilize the bubble population. This stability would be particularly useful when there are unexpected delays in production and increase in floor time results in loss of air from the batter and has a negative impact on the volume and textural properties of the crumb.
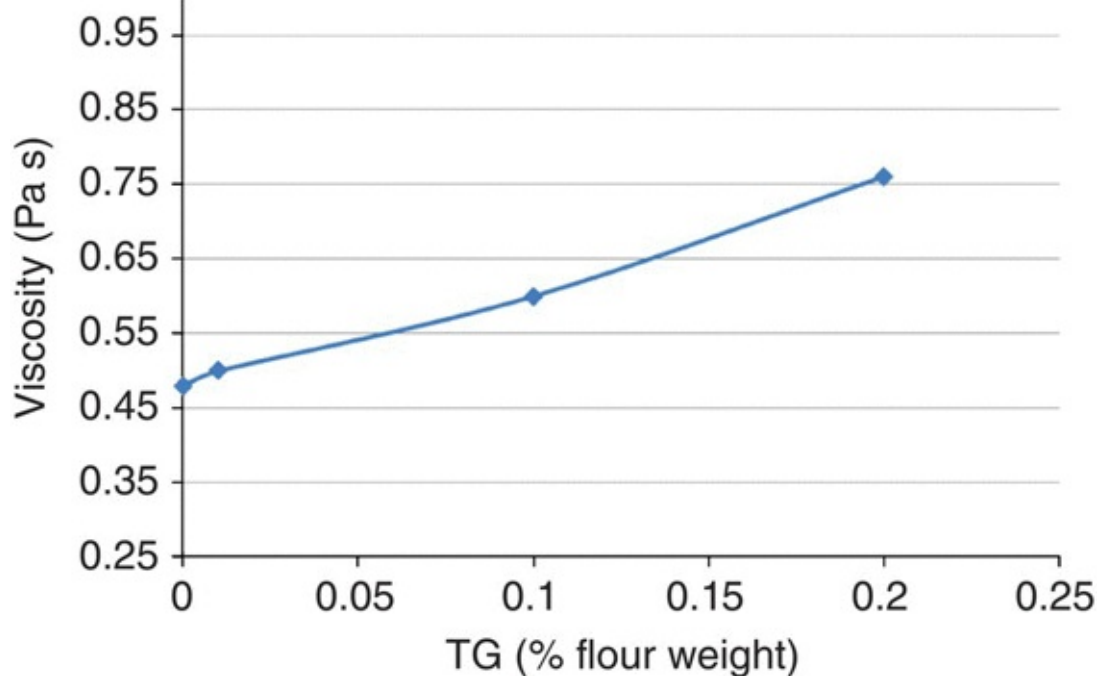
Figure 10.10 Effect of TG addition on wafer batter viscosity of a soft flour. Courtesy of Campden BRI.
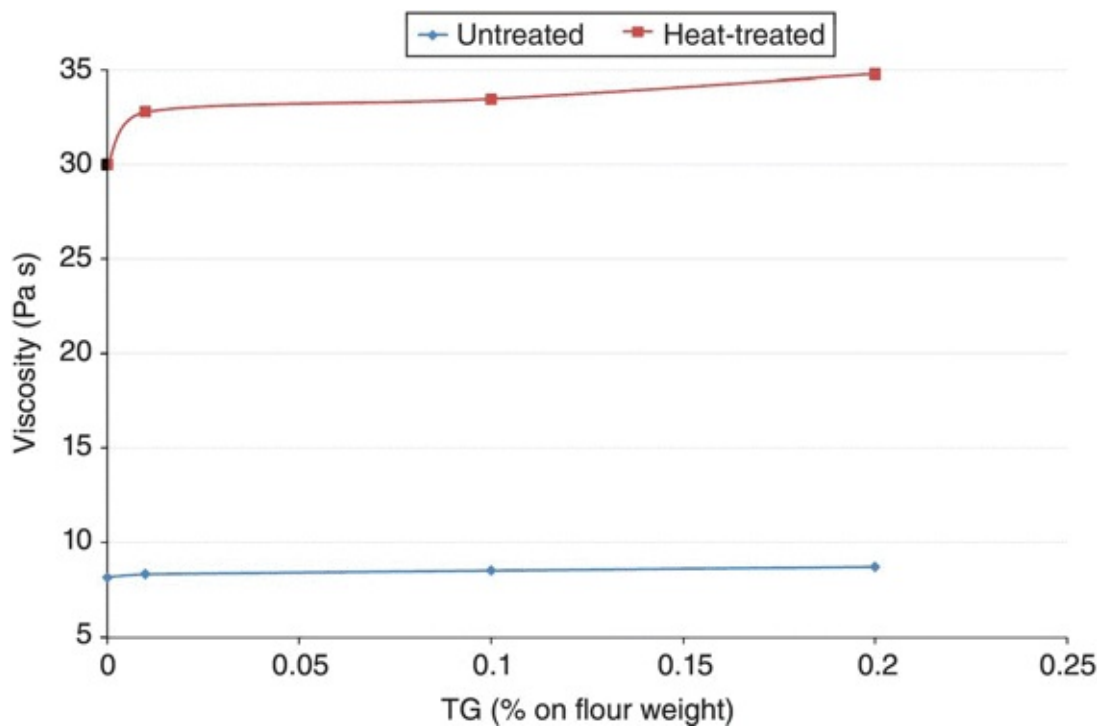
Figure 10.11 Effect of TG addition on cake batter properties. Courtesy of Campden BRI.

TG was examined in a number of model systems where it was shown to interact with wheat proteins to increase their aqueous viscosity in batters and their viscoelastic properties in doughs. The main problem with TG at present is the need to use high levels of the enzyme in the baking process. This is probably due to the slow reaction rate for the enzyme and the need to form a number of cross-links before its effect becomes obvious. The relationship between cross-links and bulk rheological changes are usually exponential in nature. There are also steric factors involved in cross-linking that are not such a problem in hydrolytic reactions such as with α-amylase and starch.

Future outlook

There has been increased pressure from consumers to reduce the amount of additives used in the production of processed foods such as bakery goods, and redox materials are one of the additives under scrutiny. There is a growing health concern, for example, about the use of reducing agents based on sulfites and action may be forthcoming about their continued use. It is important for the milling and baking community, therefore, to gain a better understanding of the role and action of improvers such as redox materials and to look for alternatives where possible. One potential alternative which is perhaps worth exploring is the use of natural plants and fruits that are rich in functional materials that act as redox agents. Examples include acerola cherry and kakadu plum, both containing elevated levels of vitamin C, as well other components that could contribute oxidation activity. This would increase the choice of materials available to produce bakery products with a healthier image, should the demand for such products increase.

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11
Sugar and Sweeteners

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Overview

Sweeteners are important ingredients in bakery products. Besides providing a sweet taste, they also affect fermentability, appearance, flavor, development, color, and texture of the finished products. There are many available choices of sugars and sweeteners, and the selected type depends on the degree of sweetness that is needed, the functions of sugar in the dough or batter being mixed, and the desired appearance or texture of the baked product (Lai and Lin 2006). According to the US Food and Drug Administration (FDA) definition, sugar is "sucrose" alone. Sucrose is the most common household sweetener, and it is one of the most important nutritive sweeteners in the food industry, available in a wide variety of types and grain sizes to meet the particular requirements of various foods. In addition to bulk, it provides a clean sweetness without off flavors and it is still the most common sweetener in baked goods (Nip 2006).Recently, however, there has been a growing interest in sucrose substitutes in the food industry as a response to public interest in low-calorie products.

Intake reduction of simple sugars is advocated principally for the treatment of diabetes, treatment and prevention of obesity, and prevention of dental caries. Diabetes, in particular, is increasing rapidly worldwide, to the extent that it has now assumed epidemic proportions. There are three prevalent types of diabetes (CDC 2013). *Type 1 diabetes* (about 5% of all diagnosed cases of diabetes in adults) develops when the body's immune system destroys pancreatic beta cells, the only cells in the body that produce the hormone insulin that regulates blood glucose; to survive, people with type 1 diabetes must have insulin delivered by injection or a pump. Type 1 diabetes usually strikes children and young adults, although disease onset can occur at any age. *Type 2 diabetes* (about 90–95% of all diagnosed cases of diabetes in adults) was previously called non-insulin-dependent diabetes mellitus or adult-onset diabetes. It usually begins as insulin resistance, a disorder in which the cells do not use insulin properly. As the need for insulin rises, the pancreas gradually loses its ability to produce it. Type 2 diabetes is associated with older age, obesity, family history of diabetes, history of gestational diabetes, impaired glucose metabolism, physical inactivity, and race and ethnicity. *Gestational diabetes* is a form of glucose intolerance diagnosed during pregnancy; it is also more common among obese women and women with a family history of diabetes. During pregnancy, gestational diabetes requires treatment to optimize maternal blood glucose levels to lessen the risk of complications in the infant.

Other types of diabetes (1–5% of all diagnosed cases) result from specific genetic conditions, surgery, medications, infections, pancreatic disease, and other illnesses. In the United States, for instance, 25.8 million people – 8.3% of the population – had diabetes in 2011; in particular, about 0.25% among those aged 20 years or younger, about 11.3% among those aged 20 years or older, and about 26.9% (10.9 million people) among those aged 65 years or older (CDC 2013). Estimates suggest that more than 6% of the population aged 20–79 years in EU countries, or 33 million people, had diabetes in 2010. Almost half of diabetic adults are aged less than 60 years. If left unchecked, the number of people with diabetes in EU countries will reach more than 37 million in less than 20 years (OECD 2012). The economic impact of diabetes is substantial: the estimated economic cost of diabetes in 2007 in the United States was US$174 billion (CDC 2013) and about 10% of total health expenditure in EU countries in 2010 (OECD 2012).

People with diabetes are at greater risk of developing cardiovascular diseases, such as heart attack and stroke if the disease is left undiagnosed or poorly controlled; they also have elevated risks for sight loss, foot and leg amputation due to damage to the nerves and blood vessels, and renal failure requiring dialysis or transplantation (OECD 2012). Approximately 60% of new cases of diabetics can be controlled adequately by diet alone, about 20% need an oral hypoglycemic drug, and another 20% of mainly younger patients, are obliged to adhere to a lifelong dietary regime. Overweight and obesity are ever-increasing problems in today's society, too. In many developed countries, more than 50% of the population is now overweight. The implications for health care are enormous. The World Health Organization, European policy makers, and national health authorities are thus taking wide-ranging measures and have asked the food industry to contribute to the global fight against overweight and obesity. Of course, the first steps in this fight are: (i) the knowledge that a combination of a balanced diet, reduced calorie intake, and physical activity is necessary for preventing overweight, obesity, and many other health diseases; and (ii) putting this knowledge into practice.

Typically, sweet baked products contain high amounts of carbohydrates, these foods being made up essentially of flours and sugars, and replacing one or both is a huge challenge, both from a technological and a nutritional point of view. However, work is in progress. As regards sweeteners, in particular, many aspects must be taken into consideration in the development of low-sugar baked goods. The reduction of sucrose can cause detectable losses in appearance, texture, flavor, and mouthfeel of the final foods; the rheological and textural properties of the products may be especially affected. Even if often considered secondary and thus little investigated, these aspects are fundamental, since a novel food adequately formulated from a nutritional and health point of view should also be pleasant and satisfactory at consumption (Mariotti and Alamprese 2012). In addition, when designing a sweet fermented food, it is necessary to know the tolerance of the specific starter microorganisms to the chemicals used as additives and to consider the modifications that the microorganisms produce on these compounds. At the same time, it is also important that the new formulations do not suffer from physical limitations, such as decomposition on heating, and that the same formulations are also able to undergo the browning effects so important to baked goods. Substitution of non-caloric or intense sweeteners for sucrose in the formulation of low-calorie products requires knowing their potency or relative sweetness and determining the amount of sweetener needed to deliver a specific level of sweetness for each product.

For all these – and many other – reasons, the development of a baked product that is lower in carbohydrates but that still tastes good is a huge challenge. However, there are many choices available nowadays. It is not the purpose of the authors to make a complete list of all these choices; as they can vary according to local legislation and in relation to ongoing findings, this list may be incomplete and out-of-date even before being printed. The chapter will focus mainly on the functional properties of sucrose and sugar substitutes, particularly in relation to their use in the production of sweet baked products.

Sugar

Sugar is a generic name referring to many carbohydrates, but it has become common usage for it to refer to one specific substance – sucrose.

Sucrose sources

Sucrose can be found in many natural foods (for example fruits and vegetables) but can only be extracted economically from sugar beet and sugar cane (roughly 60% of world sugar production is from cane and 40% from beet). Beet sugar is obtained from washed and sliced beets that are fed into a continuous diffuser and extracted with hot water; the raw juice is then subjected to different processes (carbonatation, decolorization, evaporation, centrifugation, drying) to produce the white crystals called beet sugar (James 1999). For the production of cane sugar, the harvested sugar cane is crushed and the juice squeezed out; the juice is treated to remove many of the impurities, and then evaporated to form the "*massecuite*", a mixture of sugar crystals and syrup. This mass is centrifuged to produce raw cane sugar and syrup, which is spun off and reboiled to produce another crop of raw sugar and so on, till exhaustion. After repeated dissolving, concentrating and crystallizing steps, the white cane sugar crystals are thus obtained (James 1999).

Sucrose types

Sucrose is generally available in a wide variety of types, grain sizes (roughly from 1500 to 10 μm) and colors (from white to medium or golden brown up to dark brown) (Figure 11.1), which have been developed for various areas of application.

Figure 11.1 Different sucrose types developed for various food applications.

The most commonly used sugar grain sizes are regular granulated sugars, also called fine granulated or table sugars, and confectioners or powdered sugars. In decreasing order of crystal size, sugar can be subdivided into products that may be designated as coarse, sanding, fine or extra fine, fruit, Bakers' special, superfine/ultrafine or bar, and confectioners' or powdered. The fineness is sometimes indicated by a number before an X (for example 6X, 10X, 12X), with the higher number indicating the lower particle size: for instance, a 6X powder sugar has a particle size that will allow the 93–95% passage through a 74 μm screen. Fondant and icing sugars are ultrafine powdered sugars, having grain sizes of 20 μm and smaller (for example 10X, 12X), far below the point of detection by the teeth (Nip 2006). However, there are no agreed-upon industry designations for types of sugars: the crystal size range in a given type may vary from producer to producer; not all the producers make the same range of types; different producers use different names for their products; not all types

are listed here (BeMiller 2007). In general, fine granulations are better for mixing into doughs and batters because they dissolve more quickly; fine sugars are also better for creaming with fats, because they create a finer, more uniform air cell structure and better volume. Coarse sugars are likely to leave undissolved grains, even after long mixing, and these undissolved grains appear, after baking, as dark spots on the crust, irregular texture and syrup spots. However, coarse sugar can be used in syrups, where its mixing properties are not a factor (Lai and Lin 2006). Powdered sugars are sugars ground to a fine powder, aiming to give a creamy frosting or icing on cakes or pastries; because of their fine granular size, a small amount of starch (generally 3% of cornstarch, or alternatively 1% or less of tricalcium phosphate) is usually added to avoid caking. Sugar cubes or nibs are also marketed: cubes are usually produced by mixing granulated sugar with a binding agent (usually with about 1% water), pressing into cubes and drying; nibs are agglomerates of granulated sugar crystals, made by dampening the sugar, thoroughly drying, and breaking up the resulting mass, sieving it to various sizes that are used mainly for decorating baked products (James 1999).

Liquid sugars (where all or part of the sucrose may be inverted and the total solids may range between 64 and 84%) are also available. There are advantages and disadvantages in using liquid sugars, for example ease of handling and being already dissolved, against extra water to transport and evaporate (James 1999), as well as being perishable goods with a limited shelf-life. They are available in many forms, matched to the customer's individual applications. *Invert sugar*, made by boiling sucrose with a dilute acid to turn it into its constituent monomers (glucose and fructose), is quite popular in baked products: it is hygroscopic, it has a reducing power and it resists crystallization (Lai and Lin 2006). In addition to providing sweetness, it confers some benefit by extending the mold-free shelf-life of baked products because it lowers product water activity to a greater extent than an equivalent level of sucrose (Cauvain and Young 2000).

With regards to color, other types of sugar are extensively used in bakery products, especially thanks to their aromatic, full-bodied flavor (for example brown sugar, demerara sugar, turbinado sugar, muscovado sugar). Generally, those sugars with the highest ash and organic non-sugar content are generally the ones with the stronger brown sugar flavor. *Brown sugar* consists of sugar crystals in a molasses syrup with natural flavor and color components. Many sugar refiners produce brown sugar by preparing and boiling a special syrup containing these components until brown sugar crystals form; in the final processing, the crystals are spun in a centrifuge, and the remaining syrup gives the sugar its characteristic brown color. Other refiners produce brown sugar by blending special molasses syrups (properly selected on the basis of their flavor, color, and clarity) with white sugar crystals. In this case, they are simply labeled as "light brown" or "dark brown" sugars. In addition to conferring color and flavor to the products, brown sugar has softening capabilities due to its solubility and the presence of the molasses, which contains reducing sugars. *Demerara sugar*, popular in Britain, and *turbinado sugar* – both of which are often referred to as "raw sugar" in the United States – are similar to one another in color and texture and are characterized by large grains, a pale to golden yellow to brown color, and an aromatic flavor. They can be used both to add flavor and to decorate. For their production, the molasses-rich crystals are spun in a centrifuge to dry and to remove excess plant material, leaving a coarse granule that is lighter brown or tan in color. As they are made from pure unrefined sugar cane, they contain a residue of molasses, which produces a rich and creamy texture in foods. *Muscovado sugar* and *dark muscovado sugar* are aromatic and tasty cane sugars characterized by small grains

and a moist consistency that are used mainly in baked goods, ice creams and desserts; dark muscovado sugar, in particular, has a liquorice-like flavor. They are obtained by allowing the sugar crystals to dry under low heat; muscovado does not get spun in a centrifuge.

Sucrose chemistry

Chemically, there is no difference between cane sugar and beet sugar. Sucrose ($C_{12}H_{22}O_{11}$; 342.30 g/mol) is a disaccharide composed of one molecule of glucose connected via an α-1,2 glycosidic bond to one molecule of fructose. Its structure is an exception to the general rule for structures of oligo- and polysaccharides. In sucrose, in fact, the constituent glycosyl units (an α-d-glucopyranosyl unit and a β-d-fructofuranosyl unit) are linked head-to-head, that is reducing end to reducing end, rather than the more common head-to-tail type of linkage. Since both the aldehydo group of the d-glucosyl unit and the keto group of the d-fructosyl unit are covalently bound in a mutual glycosidic bond, sucrose has no reducing end and therefore it is classified as non-reducing sugar (BeMiller 2007). It therefore cannot participate in non-enzymic browning reactions unless it is first hydrolyzed to d-glucose and d-fructose. The glycosidic bond between the two constituent sugar rings is a high-energy and unstable bond, in part due to the strained fructofuranosyl ring. Sucrose is therefore very easily hydrolyzed, even in the presence of highly diluted acid, in its two constituent sugars, originating the so-called invert sugar. Enzymes (for example invertase) also catalyze the hydrolysis of sucrose into d-glucose and d-fructose. On the other hand, sucrose is relatively stable under alkaline conditions, since it has no free carbonyl group, and acetal and ketals are stable to alkali (BeMiller 2007).

Functional properties of sucrose

From a technological point of view, the sucrose value in food products results from the unique combination of physical and chemical, including sensory, properties found in its molecule. The principal reactions of sucrose, in food manufacture or preparation, occur as reactions in solutions. Although the medium or substrate may appear to be a solid (for example bread dough, cake mixture), the sugar undergoing reaction is in solution form, dissolved in water. Sucrose can act as a sweetener (it provides a clean sweetness in baked goods with no off flavors), a preservative, a flavor and softness enhancer, a bulking agent, a source for yeast to aid fermentation in baking and brewing, a means to raise boiling or lower freezing points, an enhancer of the texture and shelf-life of certain foods, and so on. All these properties, in their unusual multiplicity and strength, combine to give sucrose its versatility as a universal sweetener. It can be used either alone or in combination with other complementary sweetening agents, but it is still the most common sweetener in baked goods. Here the focus is on these products.

Sucrose in bakery products

In addition to delivering sweetness, sucrose provides bulk, has an impact on the structure and texture of baked goods, helps to cream air into fat and maintain moisture, controls macromolecular transformations, plays a role in the emulsive-colloidal stability of the systems, modifies and enhances flavor in many cereal-based products, contributes to the spread and crispiness in cookies, acts as a softening/tenderizing ingredient, provides crust

color in products, and more (Pareyt and Delcour 2008). Some of the physical properties that are important when sucrose is used as an ingredient are solubility, hygroscopicity, particle size distribution, viscosity, and tendency to crystallize. The effect that these properties have on other components is also very important and should not be underestimated; indeed, how they influence component interactions is crucial to product quality (Davis 1995). Some examples of sucrose functionalities in baked goods are reported here.

Sucrose and sweetness

Sucrose is the standard sweetener to which all the other sweeteners are compared. Perceived sweetness is subjective and depends on or can be modified by a number of factors. The chemical and physical composition of the medium in which the sweetener is dispersed has an impact on the taste and intensity. The concentration of the sweetener, the temperature at which the product is consumed, the pH, other ingredients in the product, and the sensitivity of the taster are all important (O'Brien Nabors 2001). Sweetness response also varies with time and, in some cases, psychological effects can influence the sweet sensation; it seems to be increased by red (a warm color) and decreased by blue (a cold color), even if the concentration in the product is exactly the same. Sucrose is the usual standard (sweetness usually set equal to 1), and the intensity of the sweetness of a substance is made in relation to sucrose (*relative sweetness*). The conditions for relative sweetness comparison (for example weight basis, weight-per-volume basis, molar equivalent) must be clearly defined.

Sucrose and texture

During the mixing process, sucrose ties up water and competes with wheat flour proteins for water, preventing the full hydration of gluten and retarding its development. With the increase of sugar level in a wheat flour dough, less water is available for gluten hydration, thus requiring longer mixing times to optimally develop the gluten network (Mariotti and Alamprese 2012). In complex formulations, the initial decrease in consistency could be caused by the reaction of water with soluble solids to form a solution that remains free in the system and makes water unable to react with flour particles, and as a result increasing the time required to develop the dough (Olewnik and Kulp 1984). Doughs containing sucrose exhibit more viscous than elastic properties, probably due to the ability of sucrose to retain water, thus acting as a softening agent, producing a slack, non-cohesive dough mass (Mariotti and Alamprese 2012). With the correct proportion of sugar in the recipe, and a proper mixing time (a fundamental variable), the gluten reaches and maintains its optimum elasticity, allowing the gases produced during proofing to be held within the dough. As a result, the final leavened baked product has good volume and crumb texture.

Sucrose and yeast

Sucrose represents yeast substrate. It provides an immediately available and more utilizable source of nourishment for yeast growth, and thus for the first stage of fermentation. Depending on recipe and process conditions, sugar is broken down by yeast cells, and CO_2 is released at a faster and more consistent rate than if only the endogenous sugars and carbohydrates of wheat flour were present. *Saccharomyces cerevisiae* cells metabolize endogenous or added sugars to pyruvate via glycolysis. In the absence of oxygen, pyruvate is decarboxylated to CO_2 and acetaldehyde (which is then reduced to ethanol to regenerate NAD+). During dough mixing, water-soluble proteins, pentosans, and low molecular weight

solutes dissolve to form a mixed protein–polysaccharide aqueous phase incompatible with the hydrated gluten gel. Yeast cells are suspended in this aqueous phase, from which they take up sugars and into which they excrete metabolic by-products (Loveday and Winger 2007). In the general recipe, a sugar content of 5% will increase yeast fermentability and enhance fermentation, while when the sugar content is over 8% in the recipe, the speed of fermentation will significantly decrease (Yang 2006). Strong sugar solutions inhibit the yeast, largely because of strong osmotic pressures that affect the living cells.

Sucrose and foams or gels

Sucrose aids mechanical aeration when it is beaten with shortenings, butter or eggs. The preparation of many batters and doughs involves aeration. Sucrose stabilizes the foam produced when egg whites or whole eggs (with added sugar) are whipped during preparation of foam-type cakes (BeMiller 2007). A critical step during cake batter preparation is the blending of dry ingredients (sugar and flour) into a wet protein foam. This process involves a gentle stirring operation and the addition of sugar (small molecules) and flour (polymers) (Yang and Foegeding 2010). The sugar concentration in an angel food cake is extremely high (39.6% w/w). Based on a comparison of cakes made with and without sugar, sugar contributes to the formation of the foam network and increases cake volume for angel cakes containing a high percentage of egg white protein, but has minimal effect on the volume of angel cakes prepared from whey protein isolate (Berry and others 2009). Generally speaking, the addition of sucrose can decrease foam overrun and increase foam stability; it also makes the foam more elastic, so that the gas cells can expand. In addition, sucrose also promotes lightness by incorporating air into the shortening. In creaming, as applied to baking, shortening and crystalline sugar are mixed together so that air is incorporated. The air cells, which are stabilized by small sugar crystals at the fat–air interface, expand during baking when filled with gas from a leavening (generally chemical) agent (BeMiller 2007). The finer and more numerous the air bubbles, the finer the air cells, or grain, in the final product. Christ and others (2005) highlighted the strong influence of sucrose and sucrose concentration on the thermal and rheological properties of egg albumen proteins. Sucrose shifted the unfolding temperature of proteins to higher values so that it was necessary to employ more drastic heat treatment conditions to start the gelation process; however, heat-induced gels from egg albumen proteins with the addition of sucrose showed enhanced protein interaction, because the temperature used was higher than the denaturation temperature of ovalbumin. Such an effect was attributed to the exclusion volume effect, which facilitated aggregation and gel formation.

Sucrose and gelatinization

During baking, sugar tenderizes the matrix by absorbing liquids and delaying starch gelatinization. Spies and Hoseney (1982) studied the effect of sucrose on starch gelatinization. They noticed that, when increasing the concentration of sucrose in sugar–flour water solutions, the gelatinization temperature of starch increased. Chevallier and others (2000) also added that not only does the gelatinization temperature increase, but also the level of gelatinization decreases. However, the mechanisms with which sugar increases the starch gelatinization temperature are not yet clear. Chiotelli and others (2000) summarized by stating that the effect of sucrose on starch gelatinization is due to an interplay of factors such as lowered water activity of the system, increased volume of sucrose-

water co-solvent, antiplasticization properties of sugars relative to water, and stabilization of the granular structure due to starch–sucrose interactions. To this, Pareyt and Delcour (2008) also added the effect of water displacement by sugar. In cakes, for instance, sugar – apart from the sweetening property – has a tenderizing effect by facilitating the incorporation of air in the batter. The quality of a cake is very much related to its aerated structure, which is achieved by the incorporation of air in the batter during mixing as well as the development of bubbles during baking. A batter of low viscosity will fail to entrap sufficient air during mixing and to retain the bubbles that are formed with the liberation of gas during baking, and will result in a cake of decreased volume expansion. Hence the rheological behavior of the batter is an important factor in the aeration of the final product as it determines not only the initial incorporation of air bubbles, but also the air-holding capacity of the batter during baking (Psimouli and Oreopoulou 2012). Sucrose also has the ability to set starch gelatinization at higher temperatures by limiting water availability and therefore lowering water activity and by interacting with starch, forming bridges between starch chains. Starch gelatinization strengthens the batter structure leading to the depression of bubbles and therefore depresses the expansion of the cake batter. The delay of starch gelatinization to higher temperatures therefore allows the development of air bubbles and hence the development of a more porous structure of the end product (Psimouli and Oreopoulou 2012). Clearly, there is much to learn about the effect of sugar on starch gelatinization. This also well illustrates why substituting sucrose is not simply a matter of providing a similar sweet taste.

Sucrose and browning

The formation of color in bakery products during baking is widely known as "browning". Although typical and diverse quality features are related to each product, surface color together with its texture and flavor are the main features considered by consumers, and thus it can be used to judge the completion of baking (Purlis 2010). Browning is the result of non-enzymatic chemical reactions which produce colored compounds during the baking process; such reactions are the Maillard reaction and caramelization (Purlis 2010), which are also responsible for the aroma associated with the baked product. The Maillard reaction takes place when reducing sugars and amino acids, proteins, and/or other nitrogen-containing compounds are heated together (Fennema 1996). As sucrose is heated and inverted to glucose and fructose, the two reducing sugars react with amino acids via the Maillard reaction to produce browning and flavor compounds of importance in baked goods (Davis 1995). Caramelization is a term for describing a complex group of reactions brought on by the baking temperatures in which sucrose alone is involved. Sugar caramelizes when heated above its melting point, adding flavor and leading to surface browning which improves moisture retention in baked products. Besides the major influence of this phenomenon on the initial acceptance of products by consumers, browning is responsible for other relevant changes occurring in food during baking, such as production of flavor and aroma compounds, formation of toxic products (for example acrylamide), and decreased nutritional value of proteins (lysine losses) (Purlis 2010).

Sucrose and cracking

In biscuits and cookies, sucrose aids creaming (incorporating air into chemically leavened doughs), absorbs water (inducing spread), and crystallizes. The relatively high concentration of sugar and the relatively low content of water in some formulations result in sugar

crystallization, particularly on the surface of the cookie. As the sugar crystallizes, water and heat are released. The water evaporates resulting in crispness and surface cracking (in some cookies) (BeMiller 2007).

Sucrose and shelf-life

Sucrose provides humectancy. Its incorporation in baked products, therefore, may prevent or reduce undesirable migration of water molecules, slow down increases or decreases in the moisture content of a product and reduce water activity. In this case, sucrose can act as a preservative, being able to create an environment that retards the growth of bacteria and molds. This is particular significant for foods held at room temperature for an extended period. The reduction of sugar in specific products must be made carefully, with attention to concomitant appropriate alterations in recipes, cooking, and processing conditions.

After having presented the main functionalities of sucrose in baked goods, it becomes clearer that they cover different aspects, which must not be underestimated. It also becomes clear why it is so hard to carry out a reduction/replacement of sucrose with other sugars, sugar alcohols, or intensive sweeteners.

The perfect substitute

If the goal is the replacement of sucrose in a food product (in particular for specific diets requiring calorie restriction or for the prevention of teeth caries and decay), the substance or substances used as substitute should be competitive with sucrose, having similar – or improved – functional properties.

The ideal sweetener, for instance, should be at least as sweet as sucrose, colorless, odorless, and non-cariogenic. It should also have a clean, pleasant taste, with immediate onset without lingering: the more a sweetener tastes and functions like sucrose, the greater the consumer acceptability. For industry, if it can be processed much like sucrose with existing equipment, the more desirable it will be. The substitute should also have the following attributes: no or at least significant reduced caloric density in comparison to sucrose, on a sweetness equivalency basis; the same – or very similar – functional properties, such as provision of bulk, crystallization, hygroscopicity (humectancy), solubility and stability (in both acidic and basic conditions and over a wide range of temperatures), melting temperature, production of viscosity, reduction of water activity and the ability to impart other colligative properties; low chemical reactivity to other substances; and stability under processing, storage, transport, and food preparation conditions. Length of stability and consequently the shelf-life of the final product are also important. The sweetener must be non-toxic (safety is essential) and metabolized normally or excreted unchanged, and studies verifying its safety should be in the public domain. The final food product should taste much like the traditional one. Moreover, to be successful, a sweetener should be competitively priced with sucrose and other comparable sweeteners (O'Brien Nabors 2001; BeMiller 2007).

After presenting these "requisites", it is not surprising that no alternative substance or combination of substances meets all these criteria. The search for the perfect sweetener is continuing, but it has long been recognized that the "ideal sweetener" does not exist; even sucrose, in fact, is not perfect.

Alternative sweeteners

Sweeteners are substances with a sweet taste. Those used as alternatives to sucrose are often called "*alternative sweeteners*". Generally, sweeteners can be categorized in a number of ways: by *source*, as natural or synthetic; by *structure*, as carbohydrates or non-carbohydrates; by *degree of sweetness*, as high-intensity or low-intensity; by *caloric density*, as caloric, reduced caloric, or low-caloric; as *nutritive* (for example sucrose, fructose, glucose, syrups, honey, molasses) and *non-nutritive* sweeteners (substances that impart a sweet taste without adding appreciable calories to the product in which they are used as ingredients), and so on. To complicate matters more, some sweeteners go by several names or have brand names, and some of the newer sweeteners also have additional functions, such as being prebiotics or food fibers.

Even if the perfect sweetener probably still has to be discovered, as no sweetener up to now seems to be perfect for all uses, a multiple sweeteners approach may sometimes be of help: with several alternatives available (both to consumers and to manufacturers), each sweetener or sweeteners blend can be used in the applications for which it is best suited. The latest trend in sweeteners, in fact, is the ability of producing mixtures of sweeteners "designed" to confer the desired sweet taste with fewer calories and other functionalities to the final products.

As regards the "desired sweet taste", it must be taken into account that "perceived sweetness" is subjective, and depends on or can be modified by many factors: the chemical and physical composition of the medium, the concentration of the sweetener, the temperature at which the product is consumed, the pH, other ingredients in the product, and the sensitivity of the taster are all important (O'Brien Nabors, 2001). Moreover, when two sweeteners are blended, the perceived intensity of the mixture may be equal to (*additivity*), greater than (*synergy*) or less than (*suppression*) the sum of the individual sweetness intensities. When designing a bakery food in which sucrose has to be replaced, all these factors – as well as their interactions – must be taken into account to reach the desired sweetness of the final food.

Another aspect to consider in replacing sugar for dietetic purposes is the final "glycemic index" (GI) of the newly designed food. All dietary carbohydrates, from starch to sugar, share a basic biological property: they can be digested or converted into glucose. Digestion rate, and therefore blood glucose response, is commonly thought to be determined by the saccharide chain length (Ludwig 2002). The GI is a measure of a specific property of carbohydrate in a food or meal or diet and it is defined as "the incremental area under the blood glucose response curve of a 50 g carbohydrate portion of a test food expressed as a percentage of the response to the same amount of carbohydrate from a standard food taken by the same subject" (FAO 1998). The standard food mentioned in the definition is usually glucose in water or white bread. To avoid confusion, it is useful to express the GI relative to glucose (glucose GI = 100), and to state the standard food (glucose is preferred) and its GI (Livesey, 2003). For instance, according to databases, sucrose has a GI of 58–60, fructose of 11–23, lactose of 46–48, and maltose of 105 (GlycemicIndex 2013). The term "glycemic load", defined as the weighted average GI of individual foods multiplied by the percentage of dietary energy as carbohydrate, has been proposed to characterize the impact of foods or dietary patterns with different macronutrient composition on glycemic response (for example, a

carrot has a high GI but a low glycemic load, in contrast to a potato, in which both are high) (Ludwig 2002).

It must also be highlighted that the use of sweeteners in foods is regulated in every country; for instance, the so-called "high intensity sweeteners" that are approved in one country may not be permitted in another country; definitions or labeling information or conditions of use for some sweeteners can vary according to local regulations. Therefore, marketing and regulatory issues must be carefully checked when using sweeteners. The so-called "intense sweeteners", for instance, have been subjected to scrutiny over the years, both in relation to their safety and the intakes that result from their dietary uses. All approved intense sweeteners have undergone extensive safety testing, and have an Acceptable Daily Intake (ADI) established by bodies such as the Scientific Committee on Food (SCF) for Europe and the Joint FAO/WHO Expert Committee on Food Additives (JECFA) for international trade (Renwick 2006). The ADI, expressed in milligrams per kilogram of body weight, is the amount of a food additive that can be taken daily in the diet, even over a lifetime, without risk. It is established following toxicological testing in animals, and sometimes humans, and it is usually estimated by applying an intentionally conservative safe factor (generally a 100-fold one). Animal tests are used to determine the maximum dietary level of an additive demonstrating no toxic effects (NOAEL, "no observable adverse effect level").

Since a novel food adequately formulated from a nutritional and health point of view should also be pleasant and satisfactory to eat, a huge challenge is still represented by the detectable losses in appearance, texture, flavor, and mouthfeel of the final foods caused by sucrose reduction or substitution.

Traditional natural sweeteners

This category includes sweeteners such as honey (the only available sweetener to humans for centuries), starch syrups, molasses (by-products of sugar refining), refiner's syrup (a balanced processed syrup extracted from raw sugar), sorghum syrup (made from *Sorghum bicolor*, whose stalks are sweet and juicy), maple syrup (obtained from maple trees), raisin juice concentrate, lactose and whey powders, brown-rice syrup, barley malt, and so on. Of course, sucrose, glucose, and fructose are natural sweeteners. The same can be said for tagatose, sorbitol, and xylitol but generally they are not included in this category, as well as other "natural" compounds derived from plant extracts that belong to the so-called "high-intensity sweeteners" and will be treated later in the chapter, and other novel natural sweeteners. Only some of the "natural" sweeteners mentioned are presented here. Detailed information on the others is given by Nip (2006).

Starch sugars and syrups

A large part of the world production of corn is destined for use in the starch industry: starch is extracted from corn and further transformed into an extremely wide range of co-products, such as modified starches, dextrins, and glucose syrups that are widely used as additives in the food industry (Pagani and others 2007). Of course, other starch sources are used as well. The least converted starch products are *acid-modified starches*. A slightly more extensive modification with acid produces *dextrins*: they have film-forming and adhesive properties, increase crispness and browning in certain bakery products, and are mainly classified on the basis of their dextrose equivalent (DE), which is related to their degree of polymerization

(DP). The term DE is commonly used to describe the total reducing sugars (calculated as dextrose and expressed as a percentage of the total dry substance) in the products obtained from starch hydrolysis; by definition, the final product of starch hydrolysis, d-glucose, has a DE of 100. Hydrolysis of hot starch dispersions with either an acid or enzyme(s) to DE values lower than 20 produces *maltodextrins*. They can be digested and used by humans (so they are nutritive), they are GRAS (generally recognized as safe) food ingredients, and have many attributes: good dispersibility and solubility; provision of body, smooth texture, and pleasant mouthfeel; bland flavor; moisture control; crystallization inhibition; film formation; and low to no sweetness. These properties can vary in relation to their DE (BeMiller 2007). Hydrolysis to DE 20–35 gives a mixture of molecules that, when dried, are called corn syrup solids or glucose syrup solids. They dissolve rapidly and are mildly sweet and are used in many of the same applications as maltodextrins (BeMiller 2007). Continued hydrolysis of starch with an acid and/or enzymes produces a mixture of d-glucose, maltose, other maltooligosaccharides, and a few products that result from the formation of new glycosidic bonds. The products of this extensive starch hydrolysis are syrups known as *glucose syrups* (BeMiller 2007). The process is controlled by choosing the appropriate type of enzyme and appropriate hydrolysis conditions (pH and time of the treatments). It is therefore possible to produce both high-viscosity syrups with a low sugar concentration, and therefore low fermentation levels, as well as syrups with a high sweetening capacity, easily fermentable, and with distinct osmotic properties, where starch depolymerization is almost total (Cantarelli and Lucisano 1983). According to their DE and to their composition, glucose syrups can find different applications in bakery products. The main properties of glucose syrups, according to their DE, are reported in Table 11.1. Further enzymatic modifications cause the isomerization of the glucose into fructose, thus originating *high fructose syrups* (HFS, 42% fructose; HFCS, high fructose corn syrups, in United States). Fructose is 1.7 times as sweet as sucrose and can be used to replace sucrose in baking and various other food applications (Nip 2006), except in products such as certain cookies, in which sucrose crystallization contributes to the texture (BeMiller 2007). An *enriched fructose syrup* (55% fructose) can be obtained from HSF, by chromatographic separation of glucose and fructose, but its applications in bakery are more limited. Pure *fructose* crystals are produced from enriched fructose syrup, by seeding, crystallizing and separating crystals from the mother liquor (Nip 2006). HFS has become an increasingly common food ingredient in the past 40 years. However, there is concern that HFCS consumption increases the risk for obesity and other adverse health outcomes compared to other caloric sweeteners (Moeller and others 2009).

Table 11.1 Functional and technological properties of glucose syrups[a].

Function	Lower DE[b]	Higher DE
Bodying	←	
Thickening	←	
Viscosity	←	
Cohesiveness	←	
Fermentability		→
Browning		→
Sweetness		→
Nutritive value	←——————————————————→	
Hygroscopicity		→
Humectancy	←——————————————————→	
Emulsion stabilizer	←	
Foam stabiliser		→
Flavour enhancement		→

[a]Adapted from Jackson and Howling (1999).

[b]DE, dextrose equivalent.

Glucose, maltose and fructose

Glucose is manufactured by the complete hydrolysis of starch. The relative sweetness of d-glucose (compared to an equal concentration by weight of sucrose) is 70–80. Dextrose monohydrate is the powdered form of glucose. Crystalline glucose is used in many of the same products that utilize glucose syrups, when a dry form of the sugar is desired. *Maltose* is a reducing disaccharide composed of two glucose units. It is manufactured by liquefaction of starch followed by treatment with pullulanase and ß-amylase. The tendency to brown is about one-third that of glucose. Maltose is 40–54% as sweet as sucrose. It has a GI of 105, among the highest of any food ingredient (Godshall 2007). *Fructose*, available both as syrup and in crystalline form, is generally recognized as sweeter than sucrose, but the degree of sweetness is highly dependent on the matrix and the temperature (usually, about 160–180); it is more soluble than sucrose and dissolves more quickly; it enhances flavors, and is frequently used in bakery products (BeMiller 2007; Godshall 2007). As compared to sucrose, it enhances the hydration of starch granules and increases peak and final viscosities (BeMiller 2007).

Honey

Honey is the nectar excreted by bees after collecting the nectar from the flower pollens, and mildly processed by humans to separate foreign materials, destroy yeast, delay crystallization, and lower its viscosity (Alexander 1997). It is available in its native form or in dried mixtures, and it is used for its high sweetness and flavor attributes. It is a mixture of many different sugars, the majority being glucose and fructose, but also with small amounts of maltose and sucrose, and traces of others (Godshall 2007). Its composition depends on the types of flowers from which the nectar was collected as well as the region and climatic conditions where the flowers grew (Nip 2006). Honey is valued because it provides color, antimicrobial properties, antioxidants, flavoring, texture, and gastrointestinal benefits (enhances bifidobacterial growth), and it conveys a natural image (Godshall 2007). As it has a high fructose content, it is sweeter than sucrose and can be used as a sugar replacer in many bakery products. In baked goods, it tends to hold and contribute moisture, delaying dryness and crumbliness, thus enhancing the texture of the final product; since glucose and fructose are the main sugars, it can be easily fermented by yeast in leavened formulations; moreover, thanks to the presence of reducing sugars, honey browns easily during baking (Nip 2006). One limit is connected to its high viscosity, which makes accurate scaling difficult.

Bulk sweeteners

Bulk sweeteners (or non-nutritive sweeteners or reduced caloric sweeteners or polyols) are an important group of sweeteners consisting of ingredients that can substitute sucrose for both physical bulk and sweetness. They are used almost in the same amounts as sugar, they confer products the volume and the bulk provided by sugar, but without adding as much energy. These products, sometimes called "sugar replacers" or "bulk sweeteners", include polyols, sugar alcohols with a generally sweet taste, but with lower intensity than sucrose, and a cooling effect. Sugar replacer, sugar alcohol, hydrogenated carbohydrate, and polyol (an abridgement of polyalcohol or polyhydric alcohol) are all synonyms (Livesey 2003); however, the general "sugar replacers" is more useful for consumer communications. Polyols have fewer calories per unit mass compared to sucrose, but actual permitted calorie claims differ according to local food legislation. For food labeling purposes, the European Union has agreed that in calculating the energy value of food, the calorific value of all polyols (with the exception of erythritol) shall be 2.4 kcal/g (EC Directive 90/496/EC on nutrition labeling; EU

1990) compared to a value of 4.0 kcal/g for sugars and other carbohydrates; in the United States, values have been established on a case-by-case basis. Crystalline polyols have negative heats of solution (between -43 cal/g and -9.4 cal/g, for the most widely used ones), that are much greater than that of sucrose (-4.3 cal/g), and as a result they produce a cooling sensation in the mouth.

For food manufacturers, polyols are very versatile ingredients. They can be used to sweeten products or to perform technological functions, such acting as bulking agents, emulsifiers, stabilizers, humectants, thickeners, texturizers, glazing agents, and anticaking agents (Livesey 2003). In addition to providing sweetness, polyols can help to retain moisture in food products, lowering water activity protecting against spoilage, imparting smoothness and creaminess by inhibiting sugar crystallization, providing viscosity, assisting in retaining flavor at high temperatures, and more. Taste, appearance, nutritional quality, storage, and shelf-life can be also positively influenced by the presence of polyols (Patton and O'Brien Nabors 2011). As they do not have a reducing group, polyols do not undergo non-enzymatic browning reactions, and are relatively stable to heat and changes in pH (BeMiller 2007).

The interest in these substances has arisen recently because of the multiple potential health benefits of polyols: they are non-cariogenic (sugar-free, tooth-friendly), low-glycemic (potentially helpful in diabetes and cardiovascular disease), low-energetic and low-insulinemic (potentially helpful in obesity), low-digestible (potentially helpful in the colon), osmotic (colon-hydrating, laxative, and purifying carbohydrates), and represent a substrate for a healthy colon and intestinal tolerance. These attributes are linked through the common property of polyols of being difficult to digest or slow to metabolize yet relatively easy to ferment in the colon (Livesey 2003); so, in this sense, they can be considered as components of dietary fiber. As they have sweet tastes, at different grades, they also generally satisfy the definition of non-nutritive sweeteners. As they have fewer calories per unit mass compared to sucrose, they are usually referred to also as reduced calorie sweeteners. Moreover, since it has been determined that polyols pose no risk to human health, no ADI value has been assigned to them (BeMiller 2007). The ADI, as previously reported, is the amount of the food additive, expressed as milligrams per kilogram body weight, which can be ingested daily over a lifetime without incurring any appreciable health risk. "Acceptable" means that the expected exposure to the substance used in foods at the levels necessary to achieve the desired technological effects does not represent a hazard to health (Mortensen 2006). A problem limiting the role of polyols in human diet is their inducement of laxation when consumed in excessive doses, due to the osmotic effects of unabsorbed polyols reaching the colon (Mortensen 2006). The symptoms depend upon the specific polyol, the individual's sensitivity and the exposure time, other foods eaten at the same time, and so on. Although the FDA does not consider laxation a toxic effect, it does require that labels of products containing such sweeteners provide cautionary information (for example "excess consumption may have a laxative effect"), including serving size limitations (Levin and others 1995). Europe has the same requirements, as reported later in the chapter. The USFDA also allows the health claim that polyols do not promote dental caries.

The most widely used polyols are sorbitol, mannitol, maltitol, isomalt, lactitol, xylitol, erythritol, and hydrogenated starch hydrolyzates. Some information about them is given here and in Table 11.2.

Table 11.2 Main properties of sucrose and some bulk sweeteners[a].

Sweetener	Caloric value(kcal/g)	Sweetness[b](sucrose = 1)	ADI[c]	Heat stability (decomposes at T(°C) > ...)	Melting point(°C)	Browning on baking
Sucrose	4	1	None	>160–190	190	Yes
Bulk sweeteners						
Sorbitol	2.6[d]	0.60–0.70	None	> 160	97	No
Mannitol	1.6[d]	0.50–0.52	None	> 160	165	No
Maltitol	2.1[d]	0.74–0.95	None	> 160	150	No
Isomalt	2.0[d]	0.35–0.60	None	> 160	145–150	No
Lactitol	2.0[d]	0.35–0.40	None	> 160	122	No
Xylitol	2.4[d]	0.87–1.00	None	> 160	94	No
Erythritol	0.2	0.53–0.70	None	> 160	121	No

[a]Data from: Embuscado and Patil (2001); BeMiller (2007).

[b]Sweetness varies in different food application; these values should be regarded as approximate estimates.

[c]ADI, acceptable daily intake.

[d]The European Union has agreed that in calculating the energy value of food, the calorific value of all polyols (with the exception of erythritol) shall be 2.4 kcal/g (Directive 90/496/EEC; EU 1990); in the United States, values have been established on a case-by-case basis as reported in the table.

Sorbitol is about 60% as sweet as sucrose, and it has a moderate cooling sensation. It is the polyol produced and used in the greatest quantity. It occurs naturally in many fruits and berries, and it is produced by hydrogenation of glucose. It is quite soluble, very stable, and able to withstand high temperatures. It is commonly used as a humectant and stabilizer in bakery goods and pastry applications, extending shelf-life by maintaining the moisture content of foodstuffs. *Mannitol*, unlike sorbitol, is not a humectant. It crystallizes easily, it is only moderately soluble, and it has a high melting point. It is about 65% as sweet as sucrose and is mainly used in sugar and chocolate confectionery. *Maltitol*, made by maltose reduction, is a bulk sweetener that comes from wheat and maize, and is about 80% as sweet as sucrose. It is a white, crystalline powder very similar to sucrose, but it is digested incompletely. It is widely used in chocolate confectionery. It provides a creamy texture in baked goods such as brownies, cakes, and cookies by producing crystals that are not perceived on the tongue (BeMiller 2007). *Isomalt*, obtained from sucrose (enzymatically isomerized and then hydrogenated), has a sugar-like and mild sweetness (about half that of sucrose),

without aftertaste, and a cooling effect. It is odorless, crystalline, and non-hygroscopic; it is a non-reducing sugar, optically active. It is extremely stable with respect to chemical and enzymatic hydrolysis. It is used in baked goods often in combination with a high-intensity sweetener. *Lactitol* is made by lactose reduction and is about 40% as sweet as sugar. It passes through the small intestine almost intact, so it can be considered a prebiotic. Being a disaccharide, such as maltitol and isomalt, its colligative properties (for example, effects on water activity) are the same as those of sucrose. *Xylitol*, made by reduction of xylose, can be found in the fibers of many fruits and vegetables. It is roughly as sweet as sucrose. It has anticariogenic activity, a high negative heat of solution, and no aftertaste; for these reasons, its widest use is in confectionery. *Erythritol* is not made commercially by reduction but by a fermentation process (glucose fermentation by yeast-like fungi). It is about 65–70% as sweet as sucrose. It is non-hygroscopic and moderately soluble in water. Its sweetness profile is similar to sucrose with slight acidity and bitterness but with no detectable aftertaste. It has the highest negative heat of solution and its consumption does not produce laxation as it is rapidly absorbed in the small intestine and rapidly eliminated as well. The so-called *hydrogenated starch hydrolyzates* (HSH) are also included within polyols. They are obtained by the partial hydrolysis of corn, wheat or potato starch with acid or enzymes to produce specialized sugar syrups. By varying the conditions and extent of hydrolysis, the relative occurrence of the various mono-, di-, oligo- and polyhydrogenated saccharides in the resulting product can be tailored for various levels of viscosity, sweetness, humectancy, and other properties. Thanks to their properties (humectancy, in particular), they are used in bakery products, and the glycemic responses are lower than those of the syrups from which they are made. They can be used as bulk sugar replacers and texture modifiers (BeMiller 2007). HSH syrups do not crystallize and help to prevent crystallization in products. Their caloric content and digestibility are dependent on composition (Godshall 2007).

High-intensity sweeteners (or non-nutritive sweeteners or low-calorie sweeteners)

Another group of sweeteners consists of substances with a very intense sweet taste, that are used in small amounts to replace the sweetness of a much larger amount of sugar. The main intense sweeteners currently permitted for use in the major markets of Europe and the United States are not natural and have had to go through a food additive approval procedure.

It has been difficult to establish a general term to refer to this type of sweetener. Among professionals, the term high-potency sweetener is widely used and well understood, but consumers sometimes find this term confusing because it suggests that foods containing these ingredients are extremely sweet. The terms "alternative sweetener" or "sugar substitute" are sometimes used, but they can be confusing, as well, because they also refer to other types of sweeteners (Kroger and others 2006). The term non-nutritive sweetener could be used, but its applicability to aspartame can be questioned because aspartame is metabolized and provides dietary energy (although the quantity is negligible). Others prefer the term low-calorie sweetener because it indicates the purpose for which these ingredients are used and the types of products in which they can be found (Kroger and others 2006).

Consumers often select low- or reduced-caloric or sugar-free foods and beverages because they want the taste of sweetness without added calories or because they want to reduce the risk of tooth decay, obesity or diabetes mellitus (Kroger and others 2006). Of course, the first

choice necessary for preventing overweight, obesity, and many other health diseases, should be the practice of a varied and well-balanced diet, associated with a reduced calorie intake and physical activity. The use of high-intensity sweeteners in beverages, for instance, can effect only a minor reduction in daily energy intake. The major opportunities for energy control lie in replacing sugar in bulk foods, such as baked goods, ice cream, frozen desserts, processed foods, and condiments. In these food products, the bulk of sugar is intrinsically important to the product. Because high-intensity sweeteners provide only sweetness, combining bulking agents such as maltodextrin and polyols can provide the functional properties of sugar in foods. However, the formulations attempted have suffered from decreased palatability or from physical limitations, such as decomposition on heating, while those formulations surviving baking did not undergo the browning effect important to baked goods (Levin and others 1995). So, work is still in progress.

First of all, substitution of intense sweeteners for sucrose in low-calorie product formulation requires knowing their potency or relative sweetness or determining for each product the amount of each sweetener needed to deliver a specific level of sweetness (Bayarri and others 2007). In general, sugars and sugar-alcohols have a constant potency relative to sucrose and exhibit a linear concentration–response function; the potencies of the intense sweeteners, relative to sucrose, change with concentration and cannot then be established in absolute terms: they must be determined as a function of the desired sweetness intensity (Bayarri and others 2007). For instance, it is well known that the more viscous a fluid food or the harder a solid food is, the less sweetness is perceived upon eating. In addition, in solid foods, the big differences in composition, structure, and rheological behavior of food matrices and the well-known individual variations in the mastication process make interpretation of the perceived differences in sweetness highly difficult (Bayarri and others 2007). The matter can thus be quite tricky.

Information about the main intensive sweeteners used in baked products are given here and in Table 11.3; of course, local regulatory issues have to be checked before their use. Detailed information on the high-potency sweeteners generally used in food and beverages are given by O'Brien Nabors (2001).

Table 11.3 Main properties of sucrose and some high intensity sweeteners. (Adapted from BeMiller 2007).

Sweetener	Caloric value (kcal/g)	Sweetness[b] (sucrose = 1)	ADI[c]	Heat stability (decomposes at T(°C) > …)	Melting point (°C)	Solubility (g/100 g H_2O, 20–25 °C)	pH stability	
Sucrose	4	1	None	>160–190	190	67	Hydrolyzes at acidic and alkaline pH	N
High intensity sweeteners								
Aspartame	4[a]	160–220	0–50 (0–40)	Not stable	242–246	Sparing	3.0–5.0	S
Acesulfame-K	0	150–200	0–15 (0–9)	>200	>200	Good	5.5–7.5	I
Alitame	1.4	2000	0–1	Stable	136–147	High	Neutral pH	N
Cyclamate	0	30–60	0–11 (0–7)	Stable	170	Excellent	Stable	N
Neotame	0	7000–13000	0–2	Stable	81–83	Good	Stable	N
Sucralose	0	600	0–15	Stable	130	High	Stable	N

[a]Although aspartame provides as many calories as an equivalent weight of protein or carbohydrate, the amount used in foods and beverages is so small that the caloric contribute can be considered negligible.

[b]Sweetness varies in different food application; these values should be regarded as approximate estimates.

[c]ADI, acceptable daily intake.

Aspartame

Aspartame is made of two amino acids (l-aspartic acid and l-phenylalanine) that have no sweet taste by themselves. It is a GRAS sweetener. When hydrolyzed, it generates 4 kcal/g. The statement "contains phenylalanine" is required on the labels of all products containing aspartame (both in the United States and Europe), to safeguard all those, children in particular, suffering from phenylketonuria (PKU). PKU is an inherited disorder that increases the levels of phenylalanine in the blood; if PKU is not treated, phenylalanine can build up to harmful levels in the body, causing severe mental retardation and other serious health problems. As it is made from protein components, it is classified as a nutritive sweetener. It has a sugar-like taste, without the bitter aftertaste generally associated with artificial sweeteners (Homler 1984). It is 160–220 times sweeter than sucrose; it is stable in the dry form; in solutions, its stability is a function of pH, temperature, and time, and decomposition follows simple first-order kinetics (Nip 2006). As it can decompose under high temperature,

so it is not suitable for baking in its original form. Manufacturers thus developed an encapsulated form that can withstand heat during baking and prevents loss of sweetness intensity in baked goods (Nip 2006).

Acesulfame-K

Acesulfame-K is another GRAS sweetener. It is approximately 200 times sweeter than sucrose (based on a 3% aqueous solution) and has a clean, quickly perceptible sweet taste. It is a colorless crystalline powder, stable at normal temperature and moderate pH; it dissolves easily in water and can be added at any stage of the process; it is stable over time when stored in solids and liquids; and it is stable both in acid and alkaline conditions (Nip 2006). It is excreted completely unmetabolized, thus has no caloric value. In baking studies, no indication of decomposition of acesulfame-K was found even when biscuits with a low water content were baked at high oven temperatures for short periods; this corresponds to the observation that acesulfame-K decomposes at temperatures well above 200 °C (von Rymon Lipinski and Hanger, 2001). For all these reasons, it is highly suitable for bakery applications (usage levels ranging between 700 and 1200 ppm) (Nip 2006). As acesulfame-K combines well with suitable bulking ingredients and bulk sweeteners, it allows the production of sweet-tasting baked goods with fewer calories. In diabetic products, combinations of acesulfame-K and sugar alcohols (for example, isomalt, lactitol, maltitol, sorbitol) can provide volume and sweetness; texture and sweetness intensity can be similar to sucrose-containing products (von Rymon Lipinski and Hanger 2001).

Alitame

Alitame is formed from the amino acids l-aspartic acid and d-alanine, with a novel C-terminal amide moeity. It is this novel amide moiety that is the key to the very high sweetness potency of alitame. It is a white, crystalline, odorless, non-hygroscopic and very soluble powder (Auerbach and others 2001). It is has a clean taste, it is about 2000 times sweeter than sucrose (based on a 10% aqueous solution) and for this reason, even if it is partially metabolized (maximum 1.4 kcal/g), its caloric contribution is negligible (Nip 2006). It is sufficiently stable for use in neutral pH foods processed at high temperatures, such as sweet baked goods (Auerbach and others 2001). In accordance with its chemical structure, it can undergo chemical reaction with certain food components: in particular, high levels of reducing sugars, such as glucose and lactose, may react with alitame in heated liquid or semiliquid systems, such as baked goods, to form Maillard reaction products (Auerbach and others 2001).

Cyclamate

Cyclamate is 30–60 times as sweet as sucrose, tastes much like sucrose, and it is heat stable. In contrast to the sweet taste from sucrose, which appears quickly and has a sharp, clean cut-off, the sweetness from cyclamate builds to its maximal level more slowly and persists for a longer time (Bopp and Price 2001). It has a bitter aftertaste that can be suppressed when used in proper combination with other intensive sweeteners (for example saccharine). It was banned in the United States in 1970, because some research studies claimed that it may be carcinogenic; subsequent studies failed to confirm the original findings, so debates are still pending. It is used in Canada and in many other countries in low-calorie food products. It is a white crystalline powder, with a melting point of 169–170 °C, good aqueous solubility (1 g/7.5

ml), and a lemon-sour sweetness (Bopp and Price 2001). It is non-caloric and non-cariogenic; it is compatible with most foods and food ingredients, as well as with other sweeteners; its solubility is more than adequate for most uses, and at normal concentrations it does not change the viscosity or density of solutions; it has an excellent stability, at both high and low temperatures, over a wide pH range, and in the presence of light, oxygen, and other food chemicals; it is non-hygroscopic; however, like most non-caloric sweeteners, it does not provide the bulk, texture, or body associated with sugar (Bopp and Price 2001).

Neotame

Neotame has the highest intensity of any approved sweetener: it is reported as being 7000–13 000 times sweeter than sucrose. It is derived from and is structurally similar to aspartame but is 30–60 times sweeter; it has a clean sweet taste with no undesirable taste characteristics, and it should require no special labeling for PKU (Stargel and others 2001). It maintains stability and functionality over a range of pH, temperature, and storage times representing relevant conditions of use. It dissolves rapidly in aqueous solutions (also because of the low use levels required for sweetening); it is compatible in mixture with other sweeteners, including sugar; and it has an excellent stability in baking applications (Stargel and others 2001).

Sucralose

Sucralose is a white, crystalline, non-hygroscopic solid produced by a selective chlorination of the sucrose molecule. It is a GRAS sweetener, and it is marketed for broad use in food and beverages in many countries worldwide. Sucralose is the only high intensity sweetener made from sucrose. It is 600 times sweeter than sucrose; it is highly stable both in the solid form and in solution; it has high water solubility; it does not decompose under normal baking conditions and does not interact with the other ingredients in bakery formulations (Nip 2006). It is not metabolized by the human body and therefore it does not contribute any calories to the diet, and it is also non-cariogenic. Its applications in bakery are within the range of 170–600 ppm.

Other sweeteners

In recent years, a number of new, novel sweeteners have come on the scene, such as fructooligosaccharides (FOS), isomaltulose, lactulose, leucrose, tagatose, and trehalose, as well as a number of additional low-calorie sweeteners derived from plant extracts, such as dihydrochalcones (DHCs), glycyrrhizin, stevioside, and thaumatin (Godshall 2007). Some information on these types of sweeteners are given here. As previously stated, marketing and regulatory issues have to be checked before deciding to use one of these alternative sweeteners in baked products and/or other foods.

Fructooligosaccharides are also known as inulin syrup, oligofructose, and short-chain fructose polymers. Inulin is a heterogeneous blend of fructose polymers found widely distributed in nature as plant storage carbohydrates; oligofructose is a group of fructose polymers with a DP < 10. FOS typically refer to short-chain oligosaccharides, containing from 2 to 4 fructose molecules attached to a glucose molecule (Godshall 2007). They occur in a number of edible plants, such as chicory, onions, asparagus, and wheat; they can be obtained from natural sources, such as inulin, or derived from sucrose. Short-chain FOS, to a large

extent, escape digestion in the human upper intestine and reach the colon where they are totally fermented mostly to lactate, short-chain fatty acids (acetate, propionate and butyrate), and gas, like dietary fibers; as a consequence of their fermentation, their caloric value is approximately 2 kcal/g (Bornet and others 2002). They are excellent prebiotics. *Lactulose* is a disaccharide composed of galactose and fructose, and formed by the isomerization of lactose when milk is heated. Its relative sweetness is about 60% that of sucrose and it contains only 0.2 kcal/g. It is not broken down in the small intestine, but is fermented in the large intestine, and thus also lactulose falls into the category of prebiotics (Godshall 2007).

Isomaltulose is one of the five isomers of sucrose; it is crystalline and has a clean, sweet taste about half that of sucrose; it contains 2 kcal/g; in bakery, it is mainly used in the production of cookies and biscuits (BeMiller 2007). *Leucrose* is another isomer of sucrose, in which glucose and fructose are linked by an α1,5 bond. It has about half the sweetness of sucrose. *Tagatose*, is a ketohexose present in nature. It has a physical bulk similar to sucrose, it is about 92% as sweet as sucrose, it has about the same degree of hygroscopicity as sucrose, and it can participate in browning reactions (BeMiller 2007). It provides 1.5 kcal/g and if taken in excessive quantities can cause a laxation effect. It has a minimal effect on blood glucose and insulin levels and provides a prebiotic effect (Godshall 2007). It acts synergistically with other sweeteners and it is probably used to the greatest extent in combination with other sweeteners. It is a GRAS substance (BeMiller 2007). *Trehalose*, too, is naturally present in several common foods. It is a non-reducing disaccharide, it has low hygroscopicity and it is half as sweet as sucrose, furnishing the same number of calories. It is also a GRAS substance. Among its most prominent features is that it stabilizes proteins, protects and preserves the cell structure of foods, and maintains texture in foods during freeze/thaw cycles; it is also heat stable (Godshall 2007).

In addition to all these sweeteners, there are a number of additional low-calorie sweeteners derived from plant extracts. *Stevioside* is an example. It is a (1′-2)-linked disaccharide-containing substance present in the leaves of a small shrub *Stevia rebaudiana*. As it is a mix of several glycosides, some of which are sweet and some of which are very bitter, product purity is an important consideration. It can be isolated from dried leaves and is approximately 300 times sweeter than sucrose, with a long-lasting sweet taste. It is a highly soluble, heat- and pH-stable sweetener, with no calories and zero glycemic load. Medical research has shown benefits of stevia in treating obesity and high blood pressure. It is also considered as an effective sugar alternative for people on low-carbohydrate diets such as those with diabetes (Manisha and others 2012).

Bulking and bodying agents

A bulking agent is a substance that contributes solids to provide texture and palatability; a bodying agent is a substance that provides or improves mouthfeel (an organoleptic attribute), which is generally a function of the specific rheology perceived during chewing and swallowing (BeMiller 2007). If sugar has to be replaced with a high-intensity sweetener, another ingredient that will provide the other functionalities provided by sugar must also be added; the general term for such an ingredient is reduced-calorie bulking agent (BeMiller 2007). In general, a reduced-calorie bulking agent ingredient or a combination of ingredients might include the following attributes (depending on the specific product): ability to increase product volume (provide bulk); humectancy (ability to prevent or slow undesirable migration

of water molecules; prevention of increases or decreases in the moisture content of the product; any anticaking function is included); reduction in water activity and retardation of growth of bacteria; ability to provide sufficient shelf-life; appropriate contribution to viscosity or gel characteristics (texture, consistency); ability to provide proper crumb texture (bakery products); appropriate delay in gelatinization of starch (bakery products); appropriate spread (cookies and biscuits); appropriate surface cracking (cookies and biscuits); ability to form appropriate product color; appropriate effect on flavors and taste; proper crystallization; and freezing point depression (BeMiller 2007). Ingredients that have been investigated as reduced-calorie bulking agents (or as something that imparts the same functionality as sucrose) include polydextrose, polyols, various food gums (especially those of low molecular weight); various sources of dietary fiber, including various fruit concentrates; proteins; high-protein flours; and various oligosaccharides. However, any low molecular weight carbohydrate that has a low caloric value (that is not digested to absorbable monosaccharide units in the small intestine) contributes to fermentation in the large intestine and produces gastrointestinal discomfort (diarrhea and flatulence) to different degrees with different substances in different individuals (BeMiller 2007).

Regulations and health claims

In Europe, health and nutrition claims made in relation to food products require authorization under Regulation EC 1924/2006 (EU 2006) before they can be used in the labeling and marketing of these products in the EU. According to this regulation, "*nutrition claim*" means any claim which states, suggests or implies that a food has particular beneficial nutritional properties; "*health claim*" means any claim that states, suggests or implies that a relationship exists between a food category, a food or one of its constituents and health.

In the Annex of EC 1924/2006 (EU 2006), some important definitions related to sweeteners are reported: "low energy" is a claim that a food is low in energy, and any claim likely to have the same meaning for the consumer may only be made where the product does not contain more than 40 kcal (170 kJ)/100 g for solids or more than 20 kcal (80 kJ)/100 ml for liquids. For table-top sweeteners the limit of 4 kcal (17 kJ)/portion, with equivalent sweetening properties to 6 g of sucrose (approximately one teaspoon of sucrose), applies; "energy-reduced" is a claim that a food is energy-reduced, and any claim likely to have the same meaning for the consumer may only be made where the energy value is reduced by at least 30%, with an indication of the characteristic(s) which make(s) the food reduced in its total energy value; "energy-free" is a claim that a food is energy-free, and any claim likely to have the same meaning for the consumer may only be made where the product does not contain more than 4 kcal (17 kJ)/100 ml. For table-top sweeteners the limit of 0.4 kcal (1.7 kJ)/portion, with equivalent sweetening properties to 6 g of sucrose (approximately one teaspoon of sucrose), applies. Other definitions refer to the sugar content: "low-sugar" is a claim that a food is low in sugar, and any claim likely to have the same meaning for the consumer may only be made where the product contains no more than 5 g of sugar per 100 g for solids or 2.5 g of sugar per 100 ml for liquids; "sugar-free" is a claim that a food is sugar-free, and any claim likely to have the same meaning for the consumer, may only be made where the product contains no more than 0.5 g of sugar per 100 g or 100 ml; "with no added sugar" is a claim stating that sugars have not been added to a food, and any claim likely to have the same meaning for the consumer may only be made where the product does not

contain any added mono- or disaccharides or any other food used for its sweetening properties; if sugars are naturally present in the food, the following indication should also appear on the label: "contains naturally occurring sugars".

Regulation EC 1333/2008 (EU 2008) and the subsequent Annexes bring together in a single law all types of food additives, including sweeteners. According to this Regulation, the labeling of a table-top sweetener containing polyols and/or aspartame and/or aspartame-acesulfame salt shall bear the following warnings: (a) polyols: "excessive consumption may induce laxative effects"; (b) aspartame/aspartame-acesulfame salt: "contains a source of phenylalanine". In the Annex of this regulation, other important definitions related to sweeteners are reported. For instance, the term "sweeteners" indicates substances used to impart a sweet taste to foods or in table-top sweeteners, while "bulking agents" are substances which contribute to the volume of a foodstuff without contributing significantly to its available energy value. Each sweetener is identified by the "E-number", a systematic way of identifying different food additives: for example E420 is sorbitol, E421 mannitol, E950 acesulfame K, E951 aspartame, E952 cyclamate, E953 isomalt, E955 sucralose, E956 alitame, E960 stevioside, E961 neotame, E965 maltitol, E966 lactitol, E967 xylitol, E968 erythritol, and so on. Before a food additive is given an E-number it must first be cleared by the European Food Safety Authority (EFSA). This shows that it can be used safely in foods.

Sweeteners are approved by the FDA for use in the United States. The FDA uses two categories to classify both nutritive and non-nutritive sweeteners for regulatory purposes: some are classified as "*food additives*" (any substance, the intended use of which results directly or indirectly, in its becoming a component or otherwise affecting the characteristics of food), some others as "*generally regarded as safe*" (GRAS), and are not defined for legal purposes as food additives. A sweetener, whether nutritive or non-nutritive, can be given GRAS status on the basis of "experience based on common use in food" or a scientific consensus represented by published studies. Sorbitol and a few other polyols have GRAS status along with the natural sugars; most artificial sweeteners, however, are considered to be food additives (FDA 2013).

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12
Lipids: Properties and Functionality

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Introduction

Food lipids such as butter, margarine, cocoa butter, vegetable shortenings, and lard are widely used as functional ingredients in high-fat foods (deMan 1961; Heertje and others 1988; Shukla and Rizvi 1996; Narine and Marangoni 1999a; Campos and others 2002, 2003; Litwinenko and others 2002; Marangoni and McGauley 2003). The primary role of fats in foods is to impart sensory attributes such as creaminess, mouthfeel, spreadability, melting profile, cohesiveness, and structure (Shukla and Rizvi 1996; Sato and others 1999; Narine and Marangoni 1999a; Wright and others 2001; Sato 2001; Litwinenko and others 2002; Marangoni 2002). In many food applications, the fat component exists in a semi-solid state, in the form of a fat crystal network entrapping volumes of liquid oil (Narine and Marangoni 1999a, 1999b, 1999c; Marangoni 2002).

Lipids in baked products

Shortening refers to the ability of fat to influence the baked product by lubricating, weakening, or shortening the structure of food components so that they function in a way to provide a food product with desirable textural properties. The major functions of shortening include imparting tenderness, flavor, mouthfeel, and shortening to the gluten network. The use of shortening will also yield dough with easier handling characteristics, increased melting point, and extended shelf-life. The oil fraction of shortening supplies a moist mouthfeel, tender bite, and lubricity. On the other hand, the solid fraction of shortening contributes to the structuring of dough. The suitability of shortening for a given baking application is dependent on three main factors: the ratio of the solid to liquid phase at a given temperature, the crystal structure of the solid lipid, and the oxidative stability of the shortening.

Water and fat compete to occupy the surface of flour particle during dough mixing. If no fat is present in a dough system, flour proteins will hydrate with the readily available water and develop an extensible gluten network. When shortening is present, it is able to surround starch and protein particles, isolating them, and preventing their hydration and development. Hindering the development of the gluten network generally results in decreased dough elasticity, and baked products with softer textures.

The role and significance of shortening varies depending on its level in a product formula, as well as the type of product. When used in breads and rolls, shortening may act to tenderize the crumb while slowing the staling process, yielding products which remain softer after several days of storage compared to breads without shortening. With no shortening present, neighboring gas cell bubbles will coalesce during baking, yielding a coarser crumb structure than formulas containing shortening. Shortening has also been reported to plasticize dough, and in particular, gluten polymers present in the dough matrix (Mehta and others 2009). With increasing levels of shortening, dough will require lower levels of water to reach an equal dough consistency (Delcour and Hoseney 2010). Bread loaf volume has been reported to increase with increasing shortening concentration up to 5% (flour basis). In certain frozen dough applications, the addition of shortening has been reported to extend the shelf-life of the product by several weeks compared to control samples.

In laminated doughs, fat/shortening is incorporated into the product through a process of

rolling and folding alternating layers of dough and fat. Manipulation of laminated dough may result in dough sheets consisting of over 1000 layers of dough and fat. One of the primary goals when preparing laminated dough is to preserve the structure of alternative layers of dough and fat. Factors to consider when selecting the appropriate shortening to use for a laminated dough application include the Solid Fat Content (SFC), plasticity of the fat, complete melting point of the fat, consistency of the dough, and the desired number of folds or alternating levels in the dough. Pastry shortening should also remain flexible over a wide temperature range for the extrusion and layering of the dough. Pastries baked from laminated dough are distinguished by their distinctive flaky texture.

In high-moisture baked products such as cakes, the presence and characteristics of shortening influences the closeness of the internal grain, and the final volume of the product. These actions of shortening are related to their effects on aeration. During creaming, shortening is able to entrap air resulting in considerably increased shortening volume. When investigating the role of shortening in the stabilization of air nuclei in dough, it was shown that fat crystals are redistributed during mixing and preferentially adsorb at the numerous dough matrix–gas bubble interfaces (Mehta and others 2009). The entrapped air in the shortening provides a framework in which leavened gas can be released during the baking process. The polymorphic crystal structure of the shortening has been reported to influence the ability of shortening to aerate product systems, with shortenings crystallized into β' crystals displaying optimal aeration capabilities.

A number of studies have investigated how the level and type of shortening used in low-moisture cookie dough affects final product attributes. Abboud and others (1985) reported that when comparing three shortenings – non-emulsified shortening, shortening containing monoglycerides, and non-emulsified oil – the different shortenings did not affect cookie spread, although the level at which they were used did result in different cookie spread values. Cookie dough containing hydrogenated fats results in stiffer dough than formulations containing oil due to the greater SFI of the hydrogenated shortening. It has been reported that oil is less effective than shortening in covering the surface of flour particles as oil may be distributed through dough as droplets, whereas shortening may be distributed in thin strands, enabling a more uniform coating of flour particles (Manohar and Rao 1999). Levels of sodium dodecyl sulfate (SDS) extractable proteins were evaluated in dough and baked cookies with decreasing levels of fat in the cookie formulations. The level of extractable proteins was not different in dough with different levels of fat, although reduced fat levels in baked cookies correlated with decreased levels of SDS-extractable proteins (SDSEP). Reduced levels of SDSEP are indicative of a greater amount of protein cross-linking in cookies with lower fat levels (Pareyt and others 2011). This can be interpreted as greater gluten network development with decreasing fat levels in cookies. It can clearly be seen that fats are highly versatile and functional ingredients in baked product matrices, and influence product quality by a variety of mechanisms.

Lipid structure and properties

As fats are composed of a wide variety of triglycerides (that is, they are multicomponent systems), they do not exhibit a sharp melting or solidification temperature. Rather, fats show a wide range of melting and crystallization temperatures. This property of fats results in a high degree of variability in crystallization behavior when crystallized under various

conditions. Variables such as the cooling rate, the degree of supercooling, the presence of shear, and the storage time can all affect the resulting microstructure (deMan 1961, 1964; Heertje and others 1988; Grall and Hartel 1992; Kellens and others 1992; Heertje 1993; Fairley and others 1995; Kawanari 1996; Blaurock 1999; Narine and Marangoni 1999c; Wright and Marangoni 2002; Campos and others 2002; Litwinenko and others 2002; Marangoni and McGauley 2003). Thus, altering the crystallization conditions can result in differences in the properties of the fat crystal network at the microstructural level. These differences include the crystal size, morphology, number, and their degree of distributional order (Narine and Marangoni 1999c; Litwinenko and others 2002; Marangoni and McGauley 2003). These changes at the microscopic level affect the interactions between the particles that make up the network, which in turn influence macroscopic properties (Narine and Marangoni 1999a, 1999b, 1999c; Marangoni 2000, 2002). It is therefore important understand the relationship between microstructure and macroscopic properties.

Crystallization

Crystallization refers to the formation of solid crystals from a homogeneous solution. Crystallization in fat systems refers to the phase transition from a liquid oil, in which molecules are in random thermal motion, to a solid crystalline fat characterized by closely packed, ordered molecules. This transition is a progressive series of events beginning with the undercooling of molten fat, followed by nucleation, crystal growth, and ultimately, ripening of the resulting fat crystal network (Larson 1994; Hartel 2001). It is during this process of change that the structural elements that determine the mechanical, organoleptic, and stability properties will be defined in fat-containing products like margarine spreads and chocolate (Hartel 2001; Walstra 2003). For example, the crystallization of cocoa butter into the desirable Form V will imbue chocolate with its unique melting properties as well as with its desired snap and gloss. However, crystallization into the undesirable Form VI will be detrimental and will lead to bloom formation (Davis and Dimick 1989; Hartel 2001).

Undercooling

The major components of edible fats and oils are acylglycerols (glycerol molecules esterified with one, two, or three fatty acids (FA) for monoacylglycerols (MAG), diacylglycerols (DAG), and triacylglycerols (TAG), respectively). Individual FA can be located on different carbons within the glycerol molecule (O'Keefe 1998). As a result, natural fats are a blend of different TAG molecules, each with its own melting and crystallization properties. At temperatures above the melting point of the highest-melting component in a fat "mixture", the material exists as liquid oil. This oil is composed of TAG molecules in random thermal motion. As the temperature is decreased, the solubility of these higher-melting TAGs decrease, such that the concentration of the higher melting TAGs become supersaturated. A solution becomes supersaturated when the concentration of solutes (in this case, the higher-melting TAGs) is greater than the saturation level or the solubility limit at a particular temperature. A fat that is cooled to the point of supersaturation is undercooled or supercooled (Marangoni 2005b). The degree of undercooling (ΔT) is defined as the difference between the temperature at which a liquid fat is crystallized (T_c) and the average melting temperature of its constituent lipid species (T_m). At low degrees of undercooling ($\Delta T = 5$–$10\ °C$) and thus minimal supersaturation, the melt will exist in a metastable state. In this state, the higher-melting TAG molecules will begin to aggregate in crystal embryos that continually form, break, and re-form. In this state, the molecules from the unstable solid phase (embryos) are in equilibrium with the molecules from the liquid phase (Toro-Vazquez and Gallegos-Infante 1996). Crystallization is possible, but will not occur spontaneously unless adequate thermodynamic conditions are established (Timms 2003).

At higher ΔT, the undercooled melt is in an unstable state, generating non-equilibrium conditions (Hartel 2001). In an attempt to achieve thermodynamic equilibrium, the system will separate into a solid phase via nucleation of seed crystals (Toro-Vazquez and Gallegos-Infante 1996). The supersaturation of TAG developed through the undercooling of the melt supplies the thermodynamic drive necessary for crystallization. There is also a kinetic energy barrier for the phase transition from a disordered liquid phase to a structured crystalline solid phase (Sperling 1992; Hartel 2001; Toro-Vazquez and others 2002). Molecules in the melt

must form aggregates of TAG that exceed a given critical size parameter in order to form stable solid nuclei (Larson 1994). Crystallization onto these nuclei then occurs spontaneously from melts (Timms 2003).

Nucleation

Nucleation, as it pertains to fats, has been extensively researched and reported by several authors (Larson 1994; Aquilano and Sgualdino 2001; Hartel 2001; Rousset 2002; Timms 2003; Walstra 2003; Marangoni 2005b). TAG molecules in the undercooled, supersaturated liquid phase "come together" in a specific orientation to form embryos in the melt. For each embryo formed, the bulk Gibbs free energy change (ΔG) is favorable/negative. There is a decrease in the Gibbs free energy per unit volume (ΔG_v) in the melt. However, the creation of microscopic solid particles (that is, embryos or nuclei) in the liquid melt creates an interface that is accompanied by an unfavorable increase in the surface free energy (ΔG_s). The total Gibbs free energy change for the nucleation of a fat (ΔG_n) is thus a balance between the contribution of both changes in volume (ΔG_v) (negative) and surface area (ΔG_s) (positive).

Embryos (very small regions of the new solid phase) will continue to dynamically form and dissolve until thermodynamic conditions are suitable for the formation of nuclei. As the size of the embryos increases, the volume fraction of the solid phase will increase, resulting in a larger ΔG_v. At the same time, the increase in the crystal surface area and the interfacial free energy between the growing microcrystal phase and the melt phase will increase the ΔG_s. All this will affect the ΔG_n of the system. Changes in the ΔG_n as a function of the size of the growing embryo are illustrated in [Figure 12.1]. The net value of ΔG_n increases with respect to the size of the embryos until it reaches a maximum at the critical embryo size (r_c) and decreases from there on. The maximum value of ΔG_n obtained at the r_c is the kinetic energy barrier that must be surmounted to form stable nuclei and for nucleation to take place spontaneously. It is at or above this r_c that the unstable embryo becomes a stable nucleus. Below r_c, embryos dissociate in favor of a lower ΔG_n. Above r_c, stable nuclei form, grow, and consequently decrease the ΔG_n of the system. Nuclei are stable embryos that can eventually grow to form a crystalline solid network. The spontaneous formation of nuclei results in a decrease in the free energy level of the system accompanied by a release of latent heat (crystallization being an exothermic phase change). Nucleation is thus the formation of small TAG clusters (stable nuclei) large enough to foster the formation of a crystalline lattice structure. The crystalline network is developed by subsequent growth of the nuclei by incorporating TAGs from the melt.
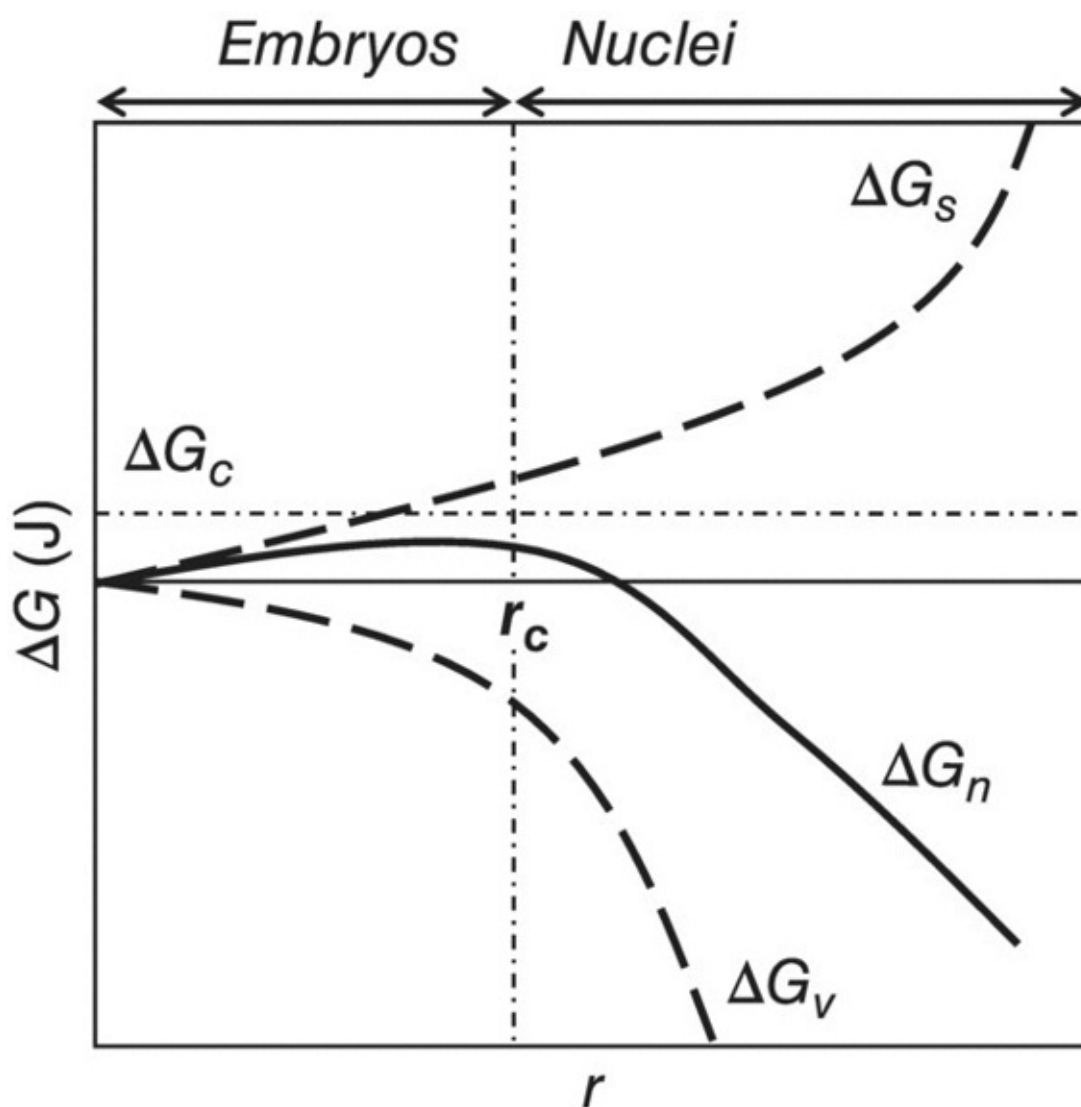
Figure 12.1 Changes in Gibbs free energy of nucleation (ΔG) as a function of the size of aggregates of TAG molecules (r) in the melt. The critical size (r_c) determines the cut-off point between unstable aggregates or embryos ($r < r_c$) and stable aggregates or nuclei ($r > r_c$). ΔG_c is the activation energy towards spontaneous nucleation.

(Adapted from Hartel (2001) and Rousset (2002)).

The number of nuclei formed per unit time and per unit volume is defined as the nucleation rate (Walstra 2003). The critical size of the embryos, as well as the nucleation rate is determined by the undercooling, ΔT and the extent of supersaturation of the system (Hartel 2001; Walstra 2003). Low crystallization temperatures increase the driving force for nucleation, as the solubility of higher melting point TAGs in lower melting point TAGs is a function of temperature (Hartel 2001). The nucleation rate is limited by molecular mobility. The degree of molecular diffusion is inversely proportional to the viscosity of the melt. At high viscosities, the mobility of TAG molecules in the melt is reduced. This affects their ability to come into contact with each other and orient themselves in proper conformations, thus limiting their ability to form new nuclei or to grow one existing nuclei (Hartel 2001; Toro-Vazquez *et al* 2002). Hence, when diffusion is impeded, the nucleation rate as well as the crystal growth rate decreases (Hartel 2001).

The phase change previously described corresponds to homogeneous nucleation. In homogeneous nucleation, nucleation is based solely on the accretion of molecules into clusters, which eventually form a stable nucleus (Hartel 2001; Walstra 2003). Homogenous

nucleation takes place only in systems with minimal or no impurities. Homogeneous nucleation requires a large driving force (Marangoni 2005b). When impurities are present, nucleation becomes heterogeneous. The energy required to form a stable nuclei is lower in the presence of impurities. This means that a lower degree of undercooling is adequate to achieve heterogeneous nucleation relative to homogeneous nucleation (Rousset 2002). Impurities present in the melt serve as templates for nucleation, as they "orient" molecules, thus reducing the number of molecular interactions required to form stable nuclei (Hartel 2001). Furthermore, impurities reduce the interfacial tension between the crystals and the melt, which further results in a lowering of ΔG_n (Marangoni 2005b). Natural fats consist of a mixture of lipid species, of which TAGs constitute the majority. Free FA and other minor components (MAGs, DAGs, and polar lipids) of different molecular weights and polarities are also present. These act as surfaces for heterogeneous nucleation (Larson 1994; Rousset 2002). In addition to impurities naturally present in fat, foreign particles that promote nucleation include dirt, dust, and rough or pitted surfaces (Hartel 2001).

These nucleation processes occur in the melt, either in the presence or absence of impurities. Nuclei can also form on the surface of existing crystals within the melt. This is known as secondary nucleation (Hartel 2001; Walstra 2003). In secondary nucleation, nuclei are generated through contact of the melt with existing crystals, as the crystal surface will induce order in the contact layer of the liquid (Larson 1994; Marangoni 2005b). Additionally, shearing of the melt can cause minute surface irregularities on existing crystals to be broken off and dispersed in the melt. These crystal pieces eventually grow into stable nuclei (Hartel 2001).

Crystal growth

Crystal growth involves both the diffusion of TAGs in the melt to the surface of nuclei and their incorporation in the correct conformation into the crystal lattice of the nucleus (Timms 2003; Marangoni 2005b). The rate of attachment of molecules onto the surface of the growing crystal is affected by the degree of undercooling (supersaturation), the conditions affecting molecular diffusion (viscosity of the melt), the geometric orientation of molecules and the total crystal surface area (Walstra 2003; Timms 2003; Marangoni 2005b). Nuclei will grow layer by layer (Rousset 2002) by incorporating molecules onto the interface via van der Waals forces (Walstra 2003). The process of incorporating TAG molecules onto an existing crystal is dynamic. Lipid species can be continually attached and detached from the crystal surface due to contact with the melt. The factors affecting lipid incorporation will determine the conditions of crystal growth (Walstra 2003). Molecules will pack closely in the newly formed solid phase so as to minimize the free energy of the new phase (Rousset 2002; Walstra 2003). Nucleation and crystal growth are not mutually exclusive processes but occur simultaneously. Formation of nuclei continues to take place while existing nuclei are growing (Timms 2003; Marangoni 2005b). Mild stirring of the crystallizing melt influences the crystallization process as it increases the rate of mass transfer and aids in the removal of the released heat of fusion from the crystal surface (Walstra 2003). Growth will continue until the crystalline phase reaches equilibrium with the surrounding oil/low-melting TAGs (Hartel 2001). The end result of crystal growth is a semi-solid, semi-crystalline material. The resulting solid/liquid mixture forms a three-dimensional fat crystal network (Marangoni 2002) in which the remaining liquid phase (oil) is immobilized through surface interactions

by the crystalline matrix (Larson 1994). It is during crystal growth that the template for the final physical properties of the resulting fat crystal network is created (Marangoni 2002).

Post-crystallization processes

Other processes take place after the formation of the solid crystalline phase has reached equilibrium. These processes include agglomeration, contraction, and ripening. Agglomeration refers to the formation of crystal aggregates (with sizes in the range of several hundred micrometers), which results in fractional crystallization (Timms 2003). Contraction of the entire crystal network has been reported for pure fats as well as for fat containing products (such as chocolate). The extent of contraction will depend on the crystal habit or morphology of the crystallized fat (Timms 2003). During the formation of a crystal network, fat molecules do not necessarily crystallize in the most thermodynamically stable phase, but may instead form into unstable transitory states (Rousset 2002). When equilibrium is attained between the solid and liquid phases after crystallization, changes in the crystalline structure can take place during storage. These processes occur so as to further minimize the surface free energy. The solid fat content does not change during these processes (Hartel 2001). This phenomenon is called recrystallization or ripening (Hartel 2001) and can involve a polymorphic transformation (Larson 1994), a change in the composition of mixed crystals, or both (Walstra 2003).

As a result of nucleation, growth, and agglomeration, the melt will exhibit compositional differences that will affect the supersaturation. As higher melting point TAGs crystallize, the supersaturation of the remaining molecules in the melt decreases, resulting in an increase of the critical radius, r_c. Small crystals ($r < r_c$) become unstable and dissolve, favoring the growth of stable large crystals ($r > r_c$) (Timms 2003). As the crystal size increases, the degree of contact between them will increase and thus lead to an increase in the attractive van der Waals forces. This is observed macroscopically as an increase in the elasticity of the fat crystal network during storage (Larson 1994).

Crystal properties

Polymorphism

Polymorphism refers to the ability of TAG molecules to pack in different geometric conformations during crystallization to yield distinct crystalline structures with identical chemical compositions but with dissimilar physical properties (density, stability, and melting point) (Sato 2001). Three different polymorphic forms have been reported for crystalline fats (Table 12.1). These are designated by the Greek letters α, β′, and β (Larson 1994; Sato 2001; Walstra 2003). From a crystallographic perspective, the existence of different polymorphic forms is due to the geometry of packing of the FA hydrocarbon chains and their angle of tilt relative to a reference plane (Marangoni 2005a). Polymorphism is determined by many factors such as the FA composition of the TAG molecules; molecular interactions which include the packing of aliphatic chains, conformation of the glycerol backbone, stacking of the methyl ends of the aliphatic chains, and olefinic interactions (in the case of mixed-acid TAGs containing unsaturated FA moieties) as well as interactions with other lipid species such as polar lipids (Sato 2001).

Table 12.1 Characteristics of the different polymorphic forms in TAG. (Adapted from Sato, Ueno & Yano (1999) and Marangoni (2005a)).

Characteristic	α Form	β′ Form	β Form
Subcell Packing	Hexagonal	Orthorhombic	Triclinic
Short Spacings	0.415 nm	0.37–0.40 and 0.42–0.43 nm	0.46 nm
Density	Least dense	Intermediate	Most dense
Melting Point	Lowest	Medium	Highest

Adapted from Sato and others 1999; Marangoni, 2005a.

When TAG molecules are transformed from the disordered liquid phase to a solid crystalline phase, the least stable α polymorph is usually the first to be formed. In this polymorph, the molecules are organized in a double chain-length structure (Larson 1994). The α polymorph has the least constraints regarding molecular incorporation into the crystal lattice (Walstra 2003). Thus, it has the lowest free energy of nucleation (Rousset 2002) and as a result, it nucleates first and grows rapidly. Further polymorphic transformations (exothermic phase transitions) will take place afterwards at various rates. The direction of polymorphic transformation is always towards the most stable form in which molecules adopt an ideal conformation and arrangement to optimize intramolecular and intermolecular interactions while achieving efficient packing of the molecules (Larson 1994). The α polymorph crystals transform into more thermodynamically stable forms (lower free energy) such as the metastable β′ form and the subsequently stable β form (Larson 1994; Walstra 2003). As such, fats are said to exhibit monotropic polymorphism, which is the existence of different solid phases where all but one are unstable (Walstra 2003).

Transformations from one polymorph to another of higher stability can be either melt-mediated or solid-mediated. In melt-mediated transformations, the metastable form melts, and the more stable form nucleates and grows from the melt. On the other hand, solid-

mediated transformations take place without going through the melt (Timms 2003). In the β form, the glycerol conformation allows the aliphatic chains in the *sn*-1 and *sn*-2 positions to form an extended chain, and the aliphatic chain in the *sn*-3 position forms a branch that is aligned parallel to the long chain formed by the aliphatic moieties on the *sn*-1 and *sn*-2 positions. This geometrical arrangement forms a triple chain-length structure (Larson 1994; Sato 2001). This results in a very effective space filling arrangement (Larson 1994), which is thermodynamically stable and has the lowest free energy relative to the other polymorphic forms (Walstra 2003). The stable β-form nucleates and grows slowly due to a high-energy barrier for nucleation (Rousset and Rappaz, 2001). The rate of melt-mediated transformation of the β form is higher than the rate for direct nucleation from the melt (Timms 2003). For this reason, nucleation of the metastable β′ form directly from the melt and subsequent transformation into the β form takes place rather than the direct nucleation of the stable β form (van Malssen and others 1999).

The presence of multiple melting species in fats was first reported almost 150 years ago. Yet, it was not until Clarkson and Malkim (1934) demonstrated the existence of different crystal forms with the aid of X-ray diffraction that this phenomenon was explained. The structure of a crystalline lattice is the result of the repetition of the unit cell in 3 dimensions (Larson 1994). The spacings in the unit cell diffract X-rays, allowing distances between the planes of the crystal network to be measured. X-rays incident on crystalline fats are deflected and two types of spacings are observed. Long spacings reflect the distances between the lipid bilayers and yield information regarding the unit cell (Walstra 2003), the fundamental unit from which the entire crystal is constructed (Marangoni, 2005b). When the three acid moieties of the TAG molecules are similar in length or unsaturation, a double chain-length structure (2 L) is obtained in which the three different FA moieties are mixed in the same chain monolayer (Larson 1994; Sato 2001). When one of the acid moieties is different from the other two in size or in unsaturation, there occurs a "sorting" of TAG molecules. One acid moiety segregates into one chain layer while the remaining two acid moieties are located in another layer, forming a triple chain-length structure (3 L) (Larson 1994; Sato 2001). As natural fats are composed of a wide variety of FA possessing various chain lengths and structures, fats typically exhibit a double chain-length structure. The triple chain-length structure is mainly observed in symmetrically mixed TAGs where saturated FA of equal length are found in the *sn*-1 and *sn*-3 positions, while an unsaturated FA is found on the *sn*-2 position, such as for cocoa butter (Sato 2001).

On the other hand, small spacings are due to the cross-sectional packing of the hydrocarbon chains and provide information regarding the subcell (de Man 1992). The subcell is the smallest spatial unit of repetition along the unit cell (Nawar 1996). The way in which ethylene groups arrange within the hydrocarbon chains of FA will result in different subcell packing that is characteristic of each polymorphic form (Marangoni 2005a). The 2 L and 3 L stacking arrangements of TAG in a fat crystal as well as an illustration of the unit cell and subcell are shown in Figure 12.2. The common subcell packing as well as the characteristics of each polymorphic form is shown in Figure 12.3.
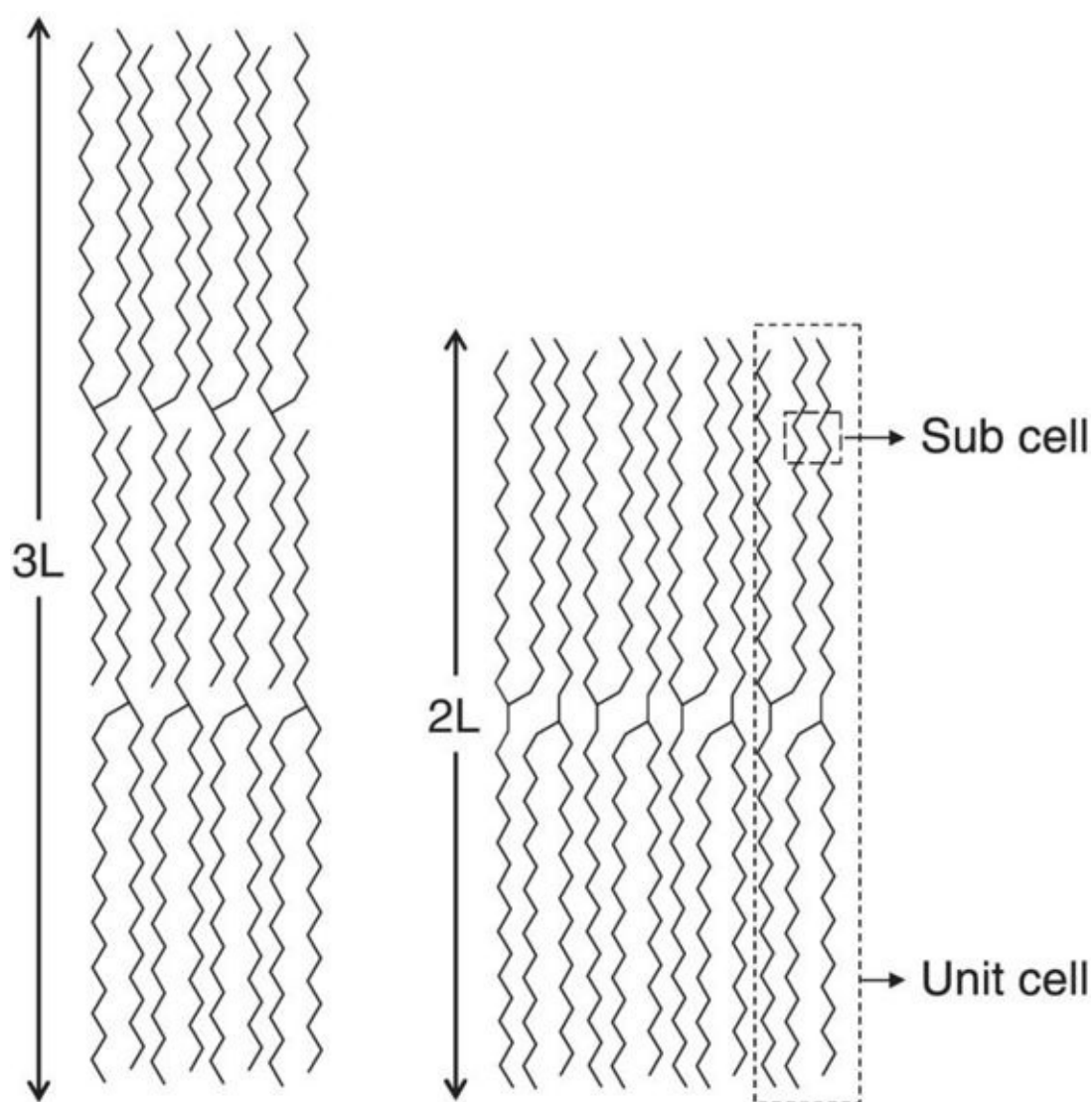
Figure 12.2 2 L and 3 L conformations of TAG crystal lamellae.
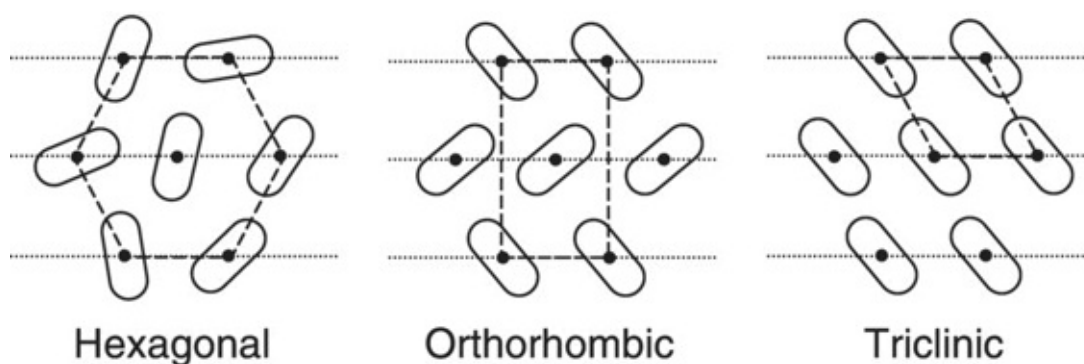
Figure 12.3 Common subcell structures in fat crystals. Each oval represents an ethylene group within the long FA chains of TAG.

(Adapted from deMan (1999)).

Crystal morphology

Crystals occur in a wide variety of shapes and sizes in a fat crystal network. The physical properties of fat products depend in part on these morphologies, which lead to the different textures in the finished product. The shape of the final crystals with their individual surfaces depends on the conditions under which the crystals were formed. Thus, a variety of crystal shapes exist even though differences are small in some cases. Changes in a crystal's shape are

related to the growth rate of the different faces. A crystal shape can vary from plate-like to needle-like to spherulitic to fibrillar. Different forms of crystals are produced when the growth parameters are different. These parameters can be temperature, speed of crystal growth, and the presence of minor components and impurities. Systems that have a high latent heat of fusion and low thermal conductivity are likely to form dendrites. Different lipid polymorphs have different shapes: spherulitic crystals are common for the β′ polymorph and plate-shaped crystals for the β form. Plate-shaped crystals of the β-polymorph can produce the perception of a grainy texture in fat (Hartel 2001). The morphology of crystals is influenced by polymorphism; however, it can be less dependent on the polymorphic form. Kellens and others (1992) observed that the microscopic appearance of tripalmitin remained the same upon being slowly transferred from α to β. Another study by Fairley and others (1995) to show the influence of polymorphic form on barrier properties of a mixture of tripalmitin and butter fat, found that the crystal morphology of the mixture affected the barrier properties in edible films. It would be expected that the barrier properties would increase in the order β > β′ > α because the density of the fat increases as the polymorphic forms transfer to a more stable form. However, the oxygen barrier properties increased in the order β > α > β′.

In another study, the microstructure of butter fat was studied through blending and interesterification with canola oil (Rousseau and others 1996). The crystal morphology of the butter fat did not change substantially after dilution with canola oil in a ratio of 90 : 10. A dense network of spherulites and ill-defined needles with no pattern was observed. Chemical interesterification of the mixture greatly influenced the morphology. The crystal network consisted of small crystals and spherulites of varying density. Addition of 20% caola oil led to substantial morphological changes in the blend. Large and dense spherulites were observed in the crystal network. Interesterification of the blend resulted in larger spherulites with small disordered platelets. Interesterification of a 50 : 50 mixture of the blend led to fewer small crystals. The results showed that the canola oil's effect on the crystal morphology are based on these assumptions: (i) canola oil has longer chain FA compared to butter fat, and canola TAGs would not be scattered throughout the butter fat crystal network; therefore, the formation of spherulites is more possible; (ii) imperfect crystals have higher surface energy and aggregation of crystals leads to a decrease in the level of the surface energy; thus, the addition of the oil to the system could facilitate the migration of crystals to form aggregates.

Lee and others (2008) studied the microstructure of a blend of fully hydrogenated soybean oil (FHSO) and palm stearin (PS) blends before and after lipase-catalyzed interesterification. They observed large rod-like spherulitic crystals in PS while long needle-like crystals were densely packed in FHSO. Both physical blending and interesterification changed the crystal morphology of the crystals. The physical blends showed needle-shaped crystals, whereas the crystals in the interesterified (IE) fat had a different shape compared to those in the physical blends. They suggested that the amount of PS influenced the structure and network of crystals, thus increasing the amount of PS induced the formation of smaller and more densely packed crystals.

Shi and others (2005) investigated the crystal morphology of model lipid systems containing low-melting and high-melting lipid classes. The high-melting lipid class or its TAG saturation level mainly dominated the morphology of crystal elements and their aggregation. For mixtures containing trisaturated long-chain FA, fat crystals were flake-shaped, and grain-like aggregates were formed. For systems containing mixed long chains, fat crystals were needle-

shaped, and typical and regular spherulites were formed. For a system containing disaturated long chains, although the elementary crystals were still needle-shaped, irregular spherulites and flocs of these spherulites were created from these elementary crystals.

Rheology of fat crystal networks

Small deformation rheology

Many plastic fats exhibit a linear viscoelastic region (LVR) at low levels of stress or strain. In fat networks, the strain typically does not exceed 0.1% before the LVR ends (Rohm and Weidinger 1993; Wright and others 2001). Within the LVR, fat networks behave as a Hookean solid where the strain is proportional to the stress (Rohm and Weidinger 1993). Beyond the LVR, strain no longer increases in a linear fashion and the network deforms irreversibly.

There are several useful parameters that may be obtained to describe a material when using small deformation rheology: the complex modulus (G*), shear storage modulus (G′), shear loss modulus (G′′) and the tangent of the phase shift or phase angle (tan δ). These values must be taken from within the LVR, and are obtained by using a dynamic oscillatory rheometer (Rao 1999). Outside the LVR, important information may be obtained such as the yield stress and yield strain.

This instrument operates by applying an oscillatory, sinusoidal stress and records the strain (Figure 12.4). The solid line corresponds to the applied stress, controlled by the instrument, and the sample's response strain appears as the dotted line. The rheometer measures the variation in strain as a function of applied stress and reports the magnitude of strain and the phase angle (δ) is the difference between two waves. If the sample is in-phase (δ = 0°), meaning that the applied stress and samples response overlap (see Figure 12.4), then it indicates that the sample is a solid and all the energy is stored in the sample. However, if they are completely out-of-phase (δ = 90°), then all the energy is lost as viscous dissipation of heat during the deformation cycle. Viscoelastic materials, which fat networks are commonly referred to, will have a δ between 0 and 90°, meaning that the samples contain both a viscous and elastic component. The storage modulus (G′) is derived from the in-phase component of the stress while the loss modulus (G′′) is derived from the out-of-phase component. The ratio of the loss and storage moduli may be expressed as the tangent of the phase angle (tan δ) (Equation 12.1):

$$\tan \delta = \frac{G'}{G''}$$

12.1
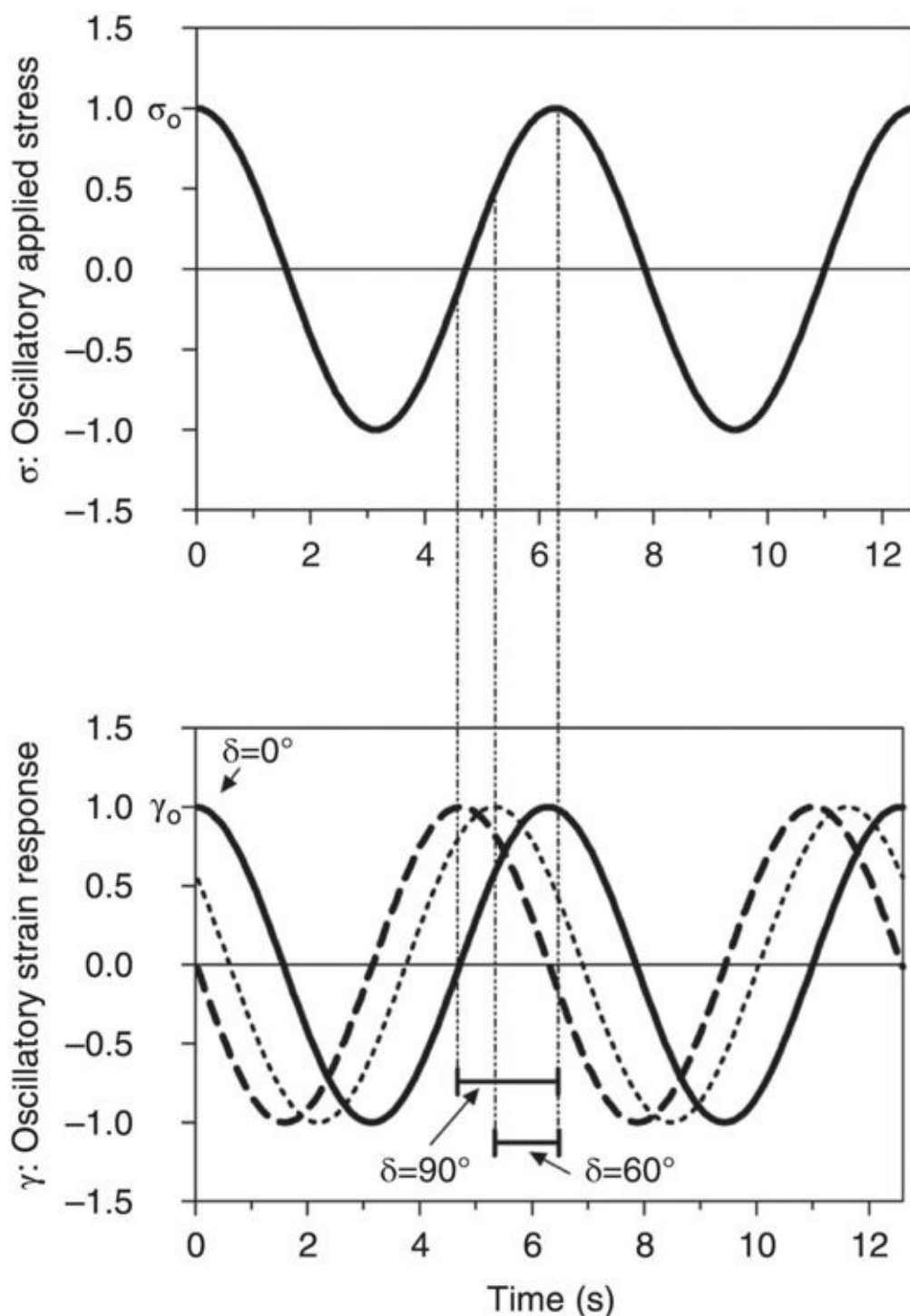
Figure 12.4 Oscillatory strain (γ) curve and the resulting oscillating stress (σ) as functions of time. Three different phase angle lags are shown.

Tan δ represents the relative balance of the viscous to elastic components of a material. Narine and Marangoni (2001) have shown these rheological measurements are associated with the hardness and spreadability of fat crystal networks. The value of tan δ becomes an excellent indicator of structural integrity for intermediate values of the phase angle. This indicates the proportion of the material's structure attributable to the crystal network and to the liquid phase.

The elastic behavior of fats may be explained by an intermolecular bonding mechanism, which provides coherence to the sample. The application of the oscillatory stress will cause a spatial displacement of structural elements. The mechanical properties of the material are influenced by the geometry of the network, as well as by the intermolecular, inter-nanostructural and inter-microstructural interactions. When the external force is removed,

the solid component has an increased energy stored in the inter- or intra-microstructural bonds that may then restore the sample to its original structure.

Large deformation rheology

Bulk fat products are considered plastic materials that are elastic when the stress or strain is below the yield stress or yield point, respectively. Above the yield stress, a plastic material is considered a fluid. In large deformation tests, the applied force is sufficient to induce permanent deformation or fracture in the sample. This measure is used to determine hardness, spreadability, cutting force and/or yield force (Wright and others 2001). There are several different instrumental setups to carry out a large deformation test. One common method is to compress a sample between two parallel plates and measure the yield force. The force required to exceed the yield stress of the network is a reliable indicator of hardness. A study using large deformation rheology indicates that samples with more saturated FA from anhydrous milk fat will have a higher solid fat content due to the elevated melting point of the species present (Narine andMarangoni 2001). As well, as solid fat content increases, so does the yield force (Rye and others 2005). Large deformation tests for fat samples correlate well with sensory tests (Rousseau and Marangoni 1998). It is, however, difficult to relate the large deformation experiments to fundamental characteristics of the microstructure of the fat crystal network because the networks are destroyed during testing.

Microstructure

The hierarchies in the structure of a fat crystal network are shown in Figure 12.5. Past work has focused on lipid composition, polymorphism, and solid fat content to interpret the mechanical strength of the network (Payne 1964; Papenhuijzen 1971, 1972; Kamphuis and Jongschapp 1985). The microstructural level of a fat crystal network will vary from 0.25 to 200 μm. It was first noted by van den Tempel (1961) that this level of structure has a large effect on the macroscopic rheological properties of the fat network. deMan (1964) as well as de Man and Beers (1987) furthered the understanding of the effect of microstructure on macroscopic hardness when examining milk fat. Marangoni's group demonstrated the importance of microstructure on the spreadablility of chemically IE and enzymatically IE milk fat and milk fat–canola oil blends (Marangoni and Rousseau 1996).
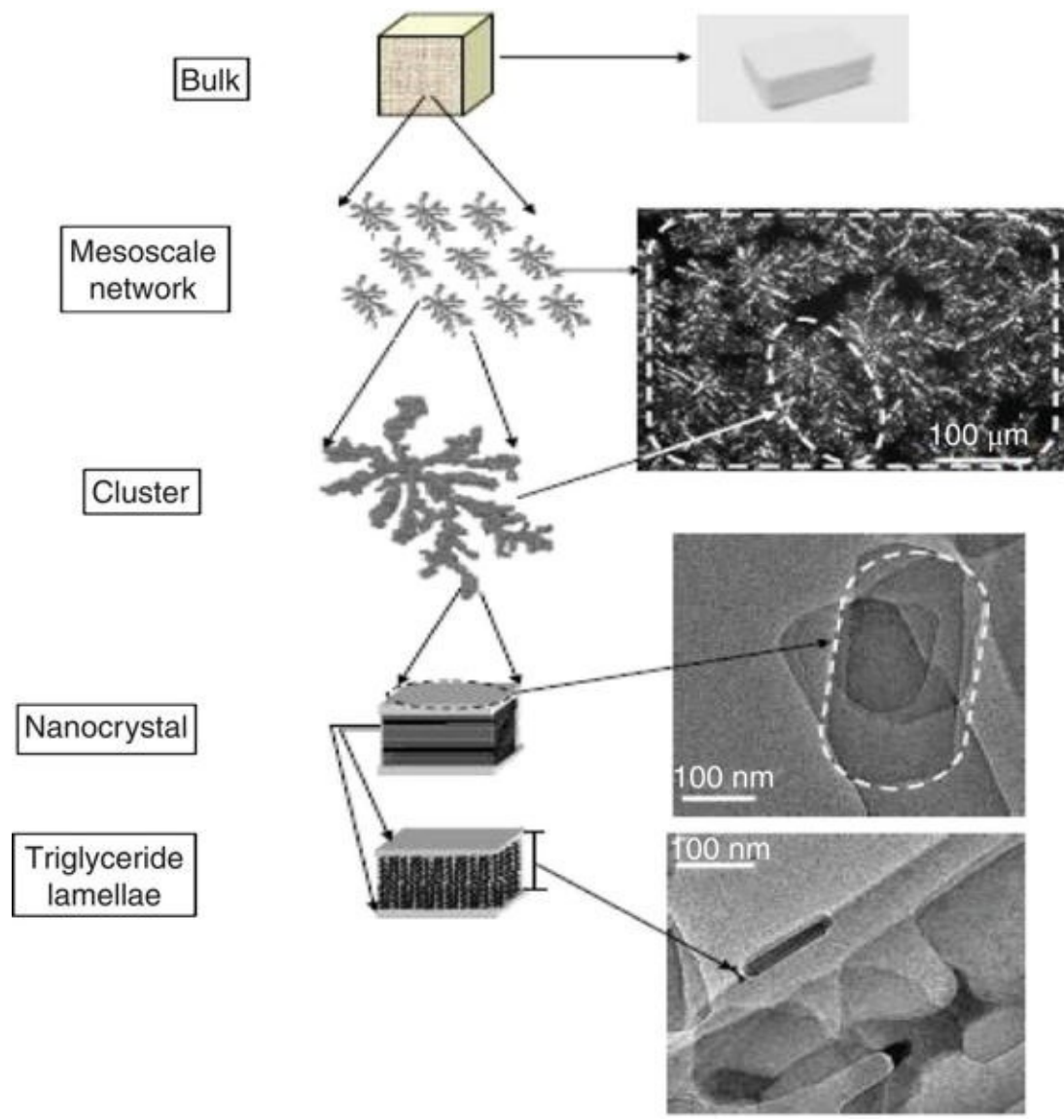
Figure 12.5 Structural hierarchy in fat crystal networks, from molecular lamellae to bulk fat through the nanoscale and mesoscale length scales.

The macroscopic properties of a fat crystal network are influenced by all levels of structural hierarchy. This includes the structure of the individual TAG and the possible FA combinations and arrangements, the crystalline structure and polymorphism of the individual crystalline units, and the morphology and agglomeration of the individual crystals,

as well as the interactions between structural elements that comprise the microstructure of the material.

An important question in the field of fat materials is that of the link between the microstructure and the observed macroscopic properties (that is, how does microstructure affect the macroscopic performance of the fat material such as rheology?). While it is obvious that the microstructure does have an effect on the macroscopic performance, the link between the two is relatively poorly understood. One of the many models that can be used to theoretically draw a link between the microstructure and the mechanical properties of a fat is the fractal model. A consecutive aggregation process forms fat crystal networks. As described previously, TAGs in the melt come together and form nuclei. Stable nuclei then grow and develop primary crystallites. Crystallites will then aggregate and form clusters. Further agglomeration of these clusters results in the formation of fractal aggregates, which form a three-dimensional network (Narine and Marangoni 1999a; Marangoni 2000, 2002; Walstra 2003). The resulting fat crystal network is then the product of fractal aggregation as it has a disordered spatial mass distribution and has statistical self-similarity. For fat crystal networks, fractal scaling is found between the size of a primary colloidal particle and a floc of primary particles (Marangoni 2005b).

Processing conditions and fat crystal network formation

The functional properties of fat containing products are dictated by the characteristics of the fat crystal network formed by its constituent lipid species (Narine and Marangoni 2002). Processing conditions directly affect the nature of the fat crystal network formed as processing conditions influence heat and mass transfer and thus structure formation (deMan 1999; Hartel 2001). A review of the effects of different processing conditions (i.e., crystallization temperature, cooling rate, and shear) on the solidification of different natural edible fats is given here.

Crystallization temperature

Crystallization temperature has a dramatic effect on the overall crystallization process, as it determines the ΔT to which a liquid fat is subjected. As mentioned earlier, ΔT will provide the thermodynamic driving force necessary to overcome the energy barrier for a phase transition. A large ΔT leads to lower free energies of nucleation, hence shorter induction times and higher crystallization rates (Campos and others 2003).

Crystallization temperatures impact the packing of TAG molecules. Stable polymorphic forms take a considerably longer time to form than metastable forms. When milk fat is crystallized at higher temperatures (low ΔT values), more stable polymorphic forms are observed (ten Grotenhuis and others 1999). van Malssen and others (1999) and Marangoni and McGauley (2003) constructed time–temperature state diagrams of the polymorphic forms found in cocoa butter from −20 to 26 °C. Their results demonstrate that as the temperature of crystallization increases, more stable polymorphic forms crystallize from the melt. Additionally, longer times are required for crystallization at higher temperatures, revealing that ΔT is critical for nucleation events.

ΔT also affects the microstructure of crystallized fats. Crystallization of a model milk fat system (Herrera and Hartel 2000c), cocoa butter (McGauley 2001), anhydrous milk fat, and lard (Campos and others 2002) at high ΔT leads to the formation of numerous small crystals, whereas fewer large crystals are observed at low ΔT. This translates into a granular microstructure at high ΔT, and the presence of spherulites at low ΔT.

Cooling rate

As early as 1964, deMan (1964) reported the effects of cooling procedures on the solid fat content, consistency, and crystal structure of milk fat. deMan (1964) compared the properties of milk fat subjected to fast, stepwise, and tempered cooling regimes. He reported that a slower crystallization process led to a decrease in solid fat content and hardness, as well as the aggregation of small crystalline particles into larger ones. Similar results have been reported elsewhere. Herrera and Hartel (2000a, 2000b, 2000c) observed the effect of cooling rate on the microstructure and elasticity of a model milk fat system. When cooled rapidly, a uniform size distribution of numerous small crystals and lower elasticity of the crystal network was observed, compared to the broad size distribution of large crystalline particles observed at slow cooling rates. Campos and others (2002) observed numerous small crystallites under rapid cooling regimes, whereas slow cooling led to a lower number of large

crystals formed in milk fat and lard. Rye (2003) observed that upon slow cooling of milk fat, the resulting fat crystal network was characterized by a small number of large crystals, lower SFC, and lower yield forces relative to those formed by fast cooling rates. The changes in mechanical properties are caused by differences in microstructure between different cooling rates. The decrease in the number of crystals which are larger in size (upon slow cooling of milk fat) result in fewer interparticle interactions and a larger amount of void spaces, leading to softer crystal networks.

The rate at which a liquid fat is cooled to a predetermined temperature will affect nucleation and polymorphism. At high cooling rates, TAG molecules have limited time to attain order in the liquid state as nucleation and growth are forced to take place on a relatively shorter time scale. Consequently, shorter induction times have been observed at higher cooling rates for cocoa butter (Rousset and Rappaz 2001), milk fat (Rye 2003; Rye and others 2005), and lard (Campos and others 2002). Higher crystallization rates have been observed under fast cooling regimes as the driving force for crystallization is higher. This translates into solidification processes taking place in a shorter time (Campos and others 2002). As a result, higher cooling rates lead to metastable polymorphs, while lower cooling rates lead to higher stability polymorphs in milk fat (ten Grotenhuis and others 1999; Rye and others 2005), cocoa butter (Rousset and others 2001), and lard (Campos and others 2002).

Shear

Shear accelerates the crystallization of synthetic polymers (Lagasse and Maxwell 1976) as it affects mass and heat transfer in the melt. Industrially, fats are sheared using scraped surface heat exchangers in the production of butter, margarine, shortenings, and chocolate, in which the fat-containing systems are crystallized while being simultaneously mixed (Walstra and others 2001, Mazzanti and others 2005). Shear enhances molecular diffusion and favors the rearrangement of molecules in the melt, which helps to overcome the kinetic barriers for nucleation and growth (Rousset and Rappaz 2001; Mazzanti, 2004). After primary nucleation has taken place, shear promotes secondary nucleation by breaking protuberances from newly formed crystals, or by sweeping off clusters of oriented molecules from growing crystal surfaces, which serve as nucleation sites (Hartel 2001; Walstra 2003). Growth of newly formed stable nuclei is affected by shear as the aliphatic chains of TAG molecules rotate faster and can therefore incorporate into the growing crystal surfaces more easily (Rousset and Rappaz 2001). Additionally, shear prevents sedimentation and aggregation of crystals by enhancing TAG mobility from the melt to the growing crystal surfaces. Moreover, shear aids in the removal of the heat of fusion, which can increase the temperature of the system and thus affect crystal growth (Walstra 2003). Shear affects the crystallization process as a whole by enhancing mass and heat transfer; promoting nucleation events; breaking clusters of crystallites, leading to the modification of the interaction between crystallites and their surroundings, which results in their orientation; and consequently affecting the characteristics of the formed fat crystal networks (Mazzanti 2004).

The effect of shear has been studied in different fat systems. When shear was applied to milk fat and milk fat fractions, Breitschuh and Windhab (1998) observed higher crystallization rates and a narrow size distribution of small crystallites, which indicated that crystallization kinetics and microstructure were affected. Herrera and Hartel (2000a, 2000c) found that agitation enhanced the nucleation of a model milk fat system, which led to the formation of

numerous small crystals. The crystallization of the studied fat system under agitation resulted in different mechanical properties for the fat crystal network obtained. This was observed as a softening of the material (Herrera and Hartel 2000b).

Similar behavior has been observed in cocoa butter. Rousset and Rappaz (2001) observed faster crystallization kinetics when shear was applied to cocoa butter melts via two concentric cylinders. In the presence of shear, the stable polymorphic Form V was formed, whereas the metastable Form IV was obtained under static conditions. Mazzanti and others (2005) also reported a reduction of phase transition times (both solid–solid, as well as melt mediated) as a function of shear not only for cocoa butter, but also for milk fat and palm oil. In the manufacture of chocolate and confections, shear is applied to the melt prior to crystallization to promote the formation of numerous small crystals. Smaller crystals are preferred for organoleptic reasons. Moreover, heat generated during the process aids in the transformation of metastable polymorphic forms to the desired Form V (Beckett 2000).

Fat replacers

Following well-documented reports on the negative cardiovascular and metabolic health effects associated with trans and saturated fat intake, there is increasing interest in developing novel semiplastic structures which do not contain undesirable hydrogenated or saturated fats for food applications. These alternatives should successfully mimic the functionality of fat crystal networks that contain trans and saturated fats.

A strategy that has shown great promise is the structuring of liquid oil utilizing the properties of lyotropic liquid crystalline phases of long-chain saturated monoglycerides (Marangoni and others 2007). Utilizing this strategy, a shortening alternative consisting of a monoglyceride gel, which encapsulates high-volume fractions of liquid oil in a water matrix that is stabilized by multilamellar monostearin multilayers, has been developed (Batte and others 2007). The low saturated fat monoglyceride gel contains only 55% fat. When comparing the structured monoglyceride emulsion to other commercial lipids, it was determined that gluten aggregation kinetics were similar between IE soy shortening and the monoglyceride emulsion, and that it maintained different functional attributes than IE soy and liquid oil as determined through Farinograph, Gluten Peak Tester, and Micro Visco Amylo Graph analysis (Huschka and others 2011). Goldstein and Seetharaman (2011) reported on functional differences observed in wire cut cookie prepared with traditional all-purpose shortening compared to formulations containing the monoglyceride gel shortening alternative. Although traditional shortening displayed superior functionality in a low-moisture cookie system, knowledge of the functional gap between the shortenings can be used to develop further strategies to create healthier baked products with appealing quality attributes.

Organogelation is another novel structuring method which has been received much interest over the past decade (Co and Marangoni 2012). An organogel may be defined as organic liquid that has been entrapped within a thermoreversible, three-dimensional network (Stortz and others 2012). Network-forming structurants may be classified as low molecular weight organogelators, or as polymers (Stortz and others 2012). The addition of ethylcellulose (EC), an organogelator which is a modified biopolymer consisting of a cellulose backbone with ethoxyl substitutions at the hydroxyl groups of carbons 2, 3, or 6, was studied in cookies. Cookies were prepared incorporating 3 or 5% by weight EC with the wet ingredients of a traditional cookie recipe containing a low saturated fat shortening. Utilizing low saturated fat shortening in cookies may result in unwanted oil migration. The addition of EC reduced the amount of oil leakage compared to control cookies containing a low saturated fat shortening alternative. Oil leakage is unwanted in cookies as migrated oil may contribute to fat bloom in cookie recipes containing chocolate (Stortz and others 2012). Cookies prepared with EC and a low saturated fat shortening were reported to be low in total fat, low in saturated fat, and offered good functionality.

The complete removal of the fats or oils from a baked product is not possible due to drastic altering of the products original attributes, although the partial replacement it feasible with other ingredients such as certain carbohydrates (Grigelmo-Miguel and others 2001). Zoulias and others (2002) studied the use of polydextrose, maltodextrin, inulin, and a blend of whey protein and emulsifiers to partially replaced fat in cookies. Partial fat replacement of up to 50% was achieved with the incorporation of inulin, maltodextrin, or the whey protein blend

although resulting cookies were hard, brittle, and did not expand adequately. The effect of fat replacement on cookie dough rheology and baked product attributes with polydextrose or maltodextrin was studied by Sudha and others (2007). They reported increases in dough hardness with fat replacement, and significantly improved baked texture with maltodextrin replacement. Recently, it was reported that shortening may be replaced partially, up to 20% with inulin (Rodriguez-Garcia and others 2012) to create cookies similar to control cookies with additional health benefits from the presence of inulin.

Conclusions

Lipids play a significant role in baked products. Their functional properties contribute positively to many quality attributes consumers expect in baked goods. Furthermore, the physical and structural properties of lipids have a significant impact on product attributes. Careful consideration, therefore, must be used in the production of fats and oils as the attributes of these lipids will drive their functionality within a particular product matrix.

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13
Eggs

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Introduction

The chicken's *(Gallus domesticus)* egg is a unique food material. It constitutes a source rich in valuable nutrients including proteins of exceptional biological value, phospholipids, unsaturated fatty acids, minerals, antioxidant carotenoids (for example, lutein and zeaxanthin) and vitamins A, B, D, E, and K. Furthermore, eggs with enhanced levels of a number of nutritionally important egg constituents, such as omega fatty acids, vitamin E, and so on, have been produced through feed supplementation. Shell eggs with improved health quality, through yolk fatty acid and/or other constituent manipulation, may command premium prices on the market and could be an answer to the decline in egg consumption over past decades.

Eggs are characterized as multifunctional food materials incorporated into a number of food systems, not only to increase their nutritional value, but also to improve color and flavor, and to enhance the product's emulsifying, whipping/foaming, and/or coagulation/gelation properties. Thus, the preparation and physicochemical stability of products such as salad dressings, meringue, custards, cakes, and omelets depend to a great extent on the presence of egg constituents functioning as air-inclusion agents, emulsifiers, and/or gel network formers, and contributing to the development of their unique sensory and rheological characteristics (Mine 2002).

The ability of eggs to perform as a multifunctional food ingredient stems from their mixed composition, especially that of the protein fraction, which is made up of constituents differing both in molecular size and structural flexibility. In general, the protein constituents of egg white have a globular nature and a rigid molecular structure. They can perform very effectively in aerated food systems, where the introduction of air in the form of tiny bubbles and subsequent stabilization is favored by proteins that, when adsorbed at the air–water (a/w) interface, retain an appreciable proportion of their secondary and tertiary structure. Yolk proteins, having a more flexible structure compared with those of the egg white fraction, can rapidly adsorb and rearrange at oil–water (o/w) interfaces, which is a prerequisite for efficient emulsifying performance (Shenton 1979). In addition, the presence in the yolk of high concentrations of phospholipids contribute to the emulsifying potential of yolk since they may also adsorb to the oil-droplet interface along with the lipoproteins resulting in the development of an adsorbed layer of a mixed nature. Egg coagulation/gelation upon heating is a property that characterizes both the egg white and the egg yolk, although the two fractions may differ in the appearance and the mechanical properties of the gels they produce, with the egg white forming stronger and more elastic gel networks than the yolk. However, when the yolk is stirred to break down its microstructure, which is made up of adjoining polyhedral "grains," it also forms cohesive gel structures exhibiting rubber-like properties (Woodward 1990).

The difference in functionality between the white and the yolk is the main reason for incorporating the former in systems where foaming is the target (such as meringue), while the yolk finds use in o/w dispersion systems such as mayonnaise and salad creams. Commercial egg white or yolk products, supplied to the food industry in the pasteurized liquid, frozen, or dehydrated form, are often contaminated by each other, something that may adversely influence their functionality. On the other hand, when whole egg is used as a food

ingredient, the yolk and the white constituents may have to function in the presence of each other as well as in the presence of other food ingredients, such as flour or milk proteins. Furthermore, each one of the egg fractions is made up of a diverse mixture of protein components, which may also exhibit differences both in structure and functionality. In the case of yolk, the organization of protein and lipid constituents into supermolecular structures, the low-density lipoprotein (LDL) micelles and the granules, may also affect the yolk protein functionality. The LDL micelles, due to their labile nature, are easily disorganized when heated (Anton and others 2003) or in the presence of oil droplet surfaces. The granular structures, on the other hand, are more compact and their protein constituents are more globular than those of the micellar lipoproteins; as a result, the granular structures are less prone to adsorb and rearrange at o/w interfaces (Kiosseoglou 1989). However, the presence of both intact or partially disorganized LDL micelles and yolk granules at the outer surface layer of yolk stabilized oil droplets in an emulsion may result in Pickering-type stabilization of the droplets against coalescence (Dickinson 2010).

The presence in a food system of a diverse mixture of egg proteins along with other biopolymers (for example, starch or milk proteins) may lead to phenomena such as biopolymer interaction, phase separation or, when oil is also incorporated, competitive adsorption at the o/w interface between the food protein constituents. All these effects are modulated by external parameters, such as mixing, homogenization, heating, and so on, leading to the establishment of the ultimate food structure (Kiosseoglou 2004). The structure of commercial whole egg, white, or yolk products should always differ from that of liquid yolk, the extent of structural alteration depending on the type and intensity of the processing method applied (pasteurization, sterilization, drying, freezing). This may constitute an additional obstacle to understanding the mechanism of egg constituent functionality in food systems, especially in products such as cakes and cookies, where commercially available whole egg is usually incorporated along with flour, milk, fat, sugar, and emulsifiers.

Chemistry of egg white and yolk

The liquid content (egg magma) of shell eggs is made up of two distinct fractions clearly separated by the vitelline membrane: (i) the white or albumen and (ii) the yolk, which represent about 56–61% and 27–32% of the total shell egg weight, respectively. The presence of the vitelline membrane between the two fractions aids in the complete separation of one from the other by hand. In modern, highly mechanized egg breaking and fraction separation production lines, on the other hand, complete separation is possible only for the preparation of yolk-free albumen; in commercially prepared liquid yolk, there is always 15–20% albumen, due to the adherence of albumen to the vitelline membrane of the separated intact yolk (Powrie and Nakai 1985). Contamination of egg white by yolk may also take place when the vitelline membrane is accidentally punctured during the process of egg breaking and/or fraction separation. The presence of albumen in yolk may not constitute a serious problem, since the albumen proteins do not antagonize the yolk proteins in systems where emulsification and emulsion stabilization are functions solely performed by the yolk. The opposite could be disastrous where successful foam preparation (meringue) demands the complete absence of the yolk constituents from the white. Inferior foaming performance of egg albumen contaminated with yolk results because the presence of yolk lipids – even at very low concentrations – may inhibit protein adsorption at the a/w interface and prevent the formation of a protein interfacial film, thus destabilizing the foam bubbles (Damodaran 1997).

A discussion on the molecular basis of the technologically important functional properties of egg and its products (frozen or spray-dried whole egg, white or yolk) should be based on an adequate understanding of egg composition and structure, but mainly of the physicochemical properties of its constituent proteins, which seem to play a key role in systems where emulsification, foaming or gelation effects are the main determinants of the final product structure and stability.

Egg white composition and structure

Egg white is a material made up of clearly distinct layers of thin and thick albumen and the chalazae. It can be considered as an aqueous solution of around 40 proteins of globular nature and one sulfated glycoprotein, the ovomucin, appearing mainly in the form of fibers that are responsible for the viscous, weak gel-like appearance of the white. The protein content of albumen is about 9.7–10.6%, depending to a large extent on chicken age. It is a material poor in carbohydrates (around 1%) existing both in the free form and combined with proteins. The presence of free carbohydrates in egg albumen (mainly glucose) may constitute a serious problem during the preparation and/or storage of spray-dried egg, due to Maillard-type reactions that lead to product quality deterioration. Finally, the albumen is practically free of lipids (only about 0.03%), compared with the yolk (Powrie and Nakai 1985).

The functional properties of albumen (foaming, gelation ability) are intimately connected with its constituent proteins. The relative content of the most important egg white proteins and some of their characteristics are presented in Table 13.1.

Table 13.1 Composition of egg yolk. (Mine 2002. Reproduced with permission of Cambridge University Press)

Constituent	% (w/v)	Major components (relative %)
Proteins	15.7–16.6	Apovitellenin (I-VI) (37.3) Lipovitellin apoproteins (40.0) α-lipovitellin β-lipovitellin Livetins (9.3) α-livetin (serum albumin) β-livetin (α2 glycoprotein) χ-livetin (χ-globulin) Phosvitin (13.4) Biotin-binding protein (trace)
Lipids	32.0–35.0	Triglycerol (66%) Phosphatidylcholine (PC) (24) Phosphatidylethanolamine (PE) (2.8) Lysophosphatidylcholine (LPC) (0.6) Shingomyelin (0.6) Cholesterol (5.0) Others (1.0)
Carbohydrate	0.2–1.0	
Ash	1.1	

Ovalbumin, which constitutes the major egg white protein (54%, dry-mass basis), is a monomeric phosphoglycoprotein existing as three types, A_1, A_2, and A_3, which differ in the number of phosphoryl residues per molecule. The molecule contains four cysteine residues, which following adsorption of the molecule at the a/w interface and unfolding, may form disulfide bridges with cysteinyl groups of neighboring molecules, leading to the strengthening of the adsorbed ovalbumin films and possibly to improvement of foam stability (Doi and Kitabatake 1997). Disulfide bridges also form between the ovalbumin molecules following heating and molecule denaturation, and result in the formation of very strong and elastic gel network structures. During storage of eggs, formation of S-ovalbumin, a molecule exhibiting higher heat stability, takes place. The S-ovalbumin molecule is slightly more compact than native ovalbumin, and its formation may involve deamidation (Nakamura and others 1980), although the exact mechanism for transforming ovalbumin to S-ovalbumin has not currently been elucidated.

Ovotransferrin or conalbumin of egg white (12%, dry-mass basis) is an iron-binding protein with a molecular weight of 78 kDa. It is a glycosylated molecule, containing 15 disulfide bridges and exhibiting a bilobal molecular structure (Mine 1995). The protein denatures at relatively low temperatures (at around 60 °C) and may become involved in intermolecular interactions, thus taking part in the development of the egg white gel network structure upon heating.

Ovomucoid (11%, dry-mass basis) is a glycoprotein (20–25% carbohydrate content) exhibiting

trypsin inhibitory activity. It is made up of three domains, each of them containing three interdomain disulfide bonds and no sulfhydryl groups. The protein can remain very stable when heated under acidic conditions at 100 °C, but it loses its biological activity when subjected to heat treatment at 100 °C for 60 min (Matsuda and others 1982).

Lysozyme (3.4%, dry-mass basis) is a basic protein (pI ~10.7) of low molecular weight (14.3 kDa) containing four disulfide bridges. It prevents bacterial infection of eggs due to its ability to lyse Gram-negative bacteria, and it is used as a food preservative or as an anti-inflammatory agent in drugs. Because the protein has a basic character, it may become involved under suitable conditions of pH and ionic content in complex formation with ovalbumin, resulting in enhancement of the gelling properties of the ovalbumin (Arntfield and Bernatsky 1993). Changes in the electrostatic interactions between lysozyme and ovomucin have been implicated in the thinning of egg white with storage time.

Ovomucin (3.5%, dry-mass basis) is a sulfated glycoprotein (30% carbohydrate content) not soluble in water but becoming solubilized in dilute salt solutions above pH 9. It is present in egg albumen in two forms, the insoluble ovomucin obtained from whole, thick egg white and the soluble form obtained from either thick or thin white. Both the insoluble and the soluble types are composed of α- and β-ovomucin containing 15 and 50% carbohydrate and having molecular weights of 18 and 400 kDa, respectively (Doi and Kitabatake 1997). The ratio of α- to β-ovomucin in the insoluble and the soluble forms of ovomucin is 84 : 20 and 40 : 3, respectively. It is believed that egg white thinning with time is connected with the dissociation of β-ovomucin in thick egg white.

Egg yolk composition and structure

Egg yolk, representing approximately 35% of the liquid egg, is a highly complex physicochemical system containing about 50% solids. The major yolk constituents, apart from water, are proteins (15.7–16.6%) and lipids (32–35%). A fraction of yolk proteins, the livetins, which constitute about 10% of the total yolk proteins, occur in the water-soluble form, while the majority (lipoproteins, phosvitin) are combined with the yolk lipids into microparticles (mainly the LDL micelles and the granules), held in suspension in water. The yolk lipids fraction is made up of about 66% triglycerides, 28% phospholipids, 5% cholesterol, and 1% other lipids (Mine 2002) (see Table 13.1).

Intact yolk in the vitelline membrane is a system of alternating layers of light yellow and deep yellow yolk stabilized by a fragile membrane into a honeycomb structure (Burley 1976). This structure is dispersed very easily upon stirring, liberating the yolk particle components. Following centrifugation of diluted egg yolk, a clear yellow liquid, called plasma, and a precipitate consisting mainly of granules, are obtained. The plasma contains the livetins and the LDL micelles. The latter, which represent about 60% of the yolk solids, consist of approximately 85% lipids (74% triglycerides and 26% phospholipids) and 15% protein. The LDL micelles seem to be made up of a neutral lipid core surrounded by protein and phospholipids. The micellar structure is highly unstable and can be easily disorganized upon heating (Anton and others 2003) or following adsorption at o/w interfaces. In this case, the lipid core of an LDL micelle fuses with the oil phase while its protein and phospholipid constituents accumulate at the interface and form an elastic interfacial film (Shenton 1979; Kiosseoglou and Sherman 1983).

The protein fraction of micelles is a heterogeneous mixture of a number of constituents, called apolipovitellenins, which exhibit a flexible structure that enables the molecules to rapidly adsorb and rearrange at o/w interfaces, something that may explain the high emulsifying ability of LDL. The molecular weight of apolipovitellenins ranges from 19 to 225 kDa (Mine 1998). An interesting feature of the apolipovitellenins is the existence in the molecules of both sulfhydryl groups and disulfide bridges. Heating above 70 °C results in increased accessibility of the sulfhydryl groups for sulfhydryl–disulfide interchanges (Nguyen and Burley 1980), and such interactions may to some extent determine the physical and textural properties of the heated yolk (Kiosseoglou and Paraskevopoulou 2005).

The yolk granules, which represent approximately 23% of the total yolk solids, are compact particles with an average diameter of 2 μm. Their structure is disorganized, and the granular components are released in the presence of 0.34 M NaCl (Burley and Cook 1962). Two lipoproteins, the α- and β-lipovitellins, constitute the major granule components (70%), the rest being a phosphoprotein called phosvitin (16%) and the granular LDL (12%) (Burley and Cook 1962). The lipovitellins have molecular weights of around 400 kDa (Bernardi and Cook 1960) and their structure is more globular than that of micellar lipoproteins. Their lipid moiety, which represents about 20% of the molecule, is held in isolated pockets at various parts of the molecule (Evans and others 1968). At pH values in the range 2–7, both the lipovitellins appear in the form of a dimer, which undergoes a reversible dimer–monomer dissociation above pH 7 or below pH 2 (Kratohvil and others 1962; Ramakrishna Rao and others 1978).

Phosvitin is a protein characterized by a high phosphorus content (10%), corresponding to around 80% of the yolk protein phosphorus content. At an alkaline pH, the molecule has an unordered conformation that changes to a more compact form following pH decrease. Inside the granular structure, the phosvitin is involved in complex formation with the lipovitellins (Li-Chan and others 1995).

Functional properties of egg in food systems

Egg constituents as emulsifying agents

The preparation and physicochemical stability of a number of traditional food products such as salad creams, mayonnaise, and egg-based creams and sauces depend to a large extent on the presence in the food system of either whole egg or yolk. The main function of egg constituents is the formation of tiny oil droplets, through adsorption and interfacial tension reduction, followed by droplet stabilization against coalescence over long periods of storage. In certain baked products such as cakes, egg constituents may have to perform multiple functions, including emulsification and stabilization of fat in the cake batter or during the baking process.

The emulsifying behavior of yolk is dominated by the protein constituents of the yolk particles (LDL micelles and granules) and seems to depend on various intrinsic factors such as protein structure and hydrophobicity and the stability of yolk particle structure, as well as on external parameters such as pH, NaCl, severity of heat or other treatment, and the presence of synthetic emulsifiers in the system. LDL micelles, as a result of their very labile nature, are very easily disorganized when they come into contact with oil droplet surfaces, followed by spreading of the apovitellenin molecules at the interface, a process favored by their high molecular flexibility and surface hydrophobicity (Shenton 1979). A number of LDL apovitellenin constituents may, however, become excluded from the interface, due to competitive adsorption effects taking place between the LDL protein components. Additionally, protein–lipid interactions at the interface may result in the formation of an adsorbed film of a mixed nature, in which both the apovitellenin molecules and surface-active yolk lipids such as phospholipids and cholesterol are accommodated (Mine 1998). Proteins from granules are also involved in interfacial film formation and emulsion stabilization. In yolk-stabilized emulsions, protein constituents originating from both the LDL micelles and the granules are found at the oil droplet surface (Mine 1998; Le Denmat and others 2000). The granules may adsorb either in their native form or after disruption with NaCl, in which case, finer emulsions are produced (Anton and others 2000).

The globular proteins of yolk, the livetins, are less effective emulsifiers than the yolk lipoproteins and are excluded from the interface in the presence of the latter. As Shenton (1979) reported, only 20% of the total livetin fraction was adsorbed at the interface of oil droplets in artificial cream emulsions stabilized by egg and milk proteins. In conclusion, the surface layer of yolk-stabilized oil droplets in an emulsion is expected to be made up of a number of protein constituents and phospholipids. Apolipoprotein molecules, originating from LDL micellar structure disruption, seem to play a dominant role in the development of the surface layer. These proteins combined with the phospholipids tend to form the primary surface layer around the oil droplets, while intact LDL micelles and partially disrupted or intact yolk granules as well as livetins seem to combine in the build-up of a secondary surface layer that offers steric stabilization to the droplets. Yolk protein adsorption at the o/w interface is so strong that their displacement by low molecular weight emulsifiers of high surface activity such as Tween is impossible and only a relatively small fraction of the yolk proteins, the less tightly adsorbed ones, are competitively displaced from the surface layer by

the surfactant molecules (Nikiforidis and Kiosseoglou 2007).

The emulsifying properties of the yolk are improved when the yolk is treated with phospholipase A_1 (Jin and others 2011) or phospholipase A_2 (Daimer and Kulozik 2010). Such an improvement is the result of lyso-phospholipids formation but mainly of the structural modification of yolk micelles and granules. Treatment of yolk with phospholipase D was also found to bring about an improvement in functionality (Buxmann and others 2010). This improvement may come from the conversion of the yolk phosphatidylcholine to phosphatidic acid and the higher interfacial activity of the latter as well as from the modification of the interactions between the proteins and the phospholipids in the yolk particle (micelles and granules) structures.

The egg white proteins are often referred to as effective foamers and coagulation agents. Recently, Drakos and Kiosseoglou (2009) reported that egg white proteins may also act as effective emulsifiers in the preparation of stable salad dressing emulsions when they are functioning on their own. In the presence of yolk, however, the egg white proteins are not able to adsorb and are competitively excluded from the o/w interface by the more flexible yolk lipoproteins. Non-adsorbing albumen proteins, then, may become involved in depletion flocculation effects, leading to changes in the stability and the rheological characteristics of the system (Kiosseoglou 2004). Drakos and Kiosseoglou (2008) reported that incorporation of dehydrated egg white into yolk-stabilized salad dressing emulsions enhanced oil droplet interaction and phase separation phenomena. These effects were connected with the fact that egg white proteins such as ovalbumin and ovomucin were practically absent from the surface of the oil droplets leading to an intensification of oil droplet interaction through depletion. Such phenomena may take place in emulsions where whole egg or commercial yolk, contaminated with egg white, is used as emulsifier. In food products such as ice-cream, where both egg and milk proteins are incorporated, the yolk lipoproteins may competitively displace from the oil droplet surface not only the globular β-lactoglobulin, but also the more flexible caseinate proteins. The extent of displacement depends on the nature of the oil phase (Aluko and others 1997; Mine and Keeratiurai 2000). In certain cake types where milk is incorporated, competitive adsorption may take place at the fat globule surface between the egg and the milk proteins, something that is bound to influence product characteristics.

Egg constituents in foam systems

Foams are dispersion systems of small-sized air bubbles in an aqueous continuous phase. A number of egg-based food products such as meringue, cake batter, and soufflé appear in the form of foam. Air entrapment and subsequent bubble stabilization against coalescence, drainage, and/or disproportionation, are functions solely performed by the egg white proteins. Egg yolk, on the other hand, is a poor foaming agent due to the presence of lipids, which adsorb and spread at the a/w interface, resulting in the displacement of the protein molecules. Interruption of protein–protein interactions by adsorbing lipids may also occur, leading to a decrease in interfacial film elasticity. When part of the yolk lipid is extracted with supercritical CO_2, both the foaming ability and the foam stability are significantly improved, probably because the residual fat is hidden inside the molecular structure of the yolk proteins and does not affect their foaming performance (Paraskevopoulou and others 1997).

The exceptional foaming properties of egg white are the result of the presence in the system

of a number of globular protein constituents differing in structure and functionality. Thus, certain albumen protein constituents, such as the globulins, are excellent foaming agents, followed by ovalbumin and ovotransferrin (Johnson and Zabik 1981a, 1981b). Egg white ovomucin, on the other hand, enhances foam stability by contributing to the formation at the air bubble surface of a thick membrane that prevents thinning of the liquid lamella film and drainage (which leads to bubble coalescence and foam breakdown).

Ovalbumin, being the major egg white protein, is bound to play a key role in the foaming and foam-stabilizing ability of egg. When adsorbed at the a/w interface, the ovalbumin molecules unfold and rearrange to orient their hydrophobic areas towards the oil phase. The adsorbed molecules then interact through a combination of disulfide bridges and non-covalent bonds to form a cohesive and elastic interfacial membrane. Although both covalent and non-covalent interactions are involved in interfacial film formation, the former seems to be less important for the long-term stability of the foam system (Doi and Kitabatake 1997).

The foaming properties of an isolated egg white protein are modified when the protein has to function with other egg white proteins. At a neutral pH, the basic protein lysozyme is involved in the formation of electrostatic complexes with the negatively charged proteins of the white, and this interaction may result in an enhancement of the foaming power of the mixture. Additionally, the adsorption behavior of certain egg white protein constituents at the a/w interface seems to be affected by the formation of an electrostatic complex with lysozyme (Damodaran and others 1998). As Lechevalier and others (2004) have also reported, ovotransferrin denaturation, following adsorption at the a/w interface, may differ depending on the presence of other egg white proteins. In admixture with ovalbumin, ovotransferrin molecules seem to undergo extensive structural modification at the interface, possibly due to ovotransferrin–ovalbumin interactions at the a/w interface and aggregate formation, something that was not observed in the case of ovotransferrin–lysozyme mixed solutions.

Egg white protein interactions either in bulk or at the a/w interface should be taken into consideration when trying to investigate the molecular basis of egg white protein foaming. As Lechevalier and others (2004) suggested, it is not appropriate to extrapolate from data obtained for isolated egg white proteins in order to explain the foaming behavior of the highly complex egg albumen fraction. Two relatively recently published papers (Le Floch-Fouéré and others 2009, 2010), provided evidence of synergy between ovalbumin and lysozyme molecules adsorbed from binary solutions with respect to interfacial foaming properties. The irreversibly adsorbed interfacial protein layer exhibited a stratified organization, with an ovalbumin monolayer in direct contact with the air phase and a secondary multilayer made up of lysozyme, irrespective of the order of adsorption of the two proteins. It was also concluded that the interactions between the two proteins took place as a result of their adsorption at the a/w interface and the molecular denaturation that followed and not in the bulk protein solution.

The foaming properties of egg white proteins may deteriorate following egg storage or when the liquid egg white is subjected to various processing treatments, especially those involving heat (Mine 1995). Dehydration, in particular, may result in protein denaturation, aggregation, and partial loss of functionality, a trend that may be reversed when the dehydrated material is subjected to dry-heating under controlled conditions. This improvement was connected by Nicorescu and others (2011) with the formation during heating of soluble protein aggregates and oligomers, which along with the presence in the dry-heated mixture of a minimum

amount of monomers were necessary for optimum foaming performance of the egg white protein.

Egg coagulation and gelation

Heat treatment of liquid egg results in protein denaturation followed by coagulation/gelation. The thermal setting of cake batter or egg-based creams and the development of the final product structure, therefore, depend to a large extent on the presence in the system of egg protein constituents, which unfold and interact, leading to the formation of a mixed protein gel network.

Both the liquid egg fractions, the albumen and the yolk, have the ability to form, following heating above 70 °C, gel networks that are thermally irreversible. Egg white produces very elastic gels with a milky white appearance, while the physicochemical characteristics of the yolk gels depend on the state of the yolk honeycomb structure present in intact yolk. Heating intact yolk results in a gel of crumbly texture and low strength. When the yolk structure is broken down by stirring, a gel exhibiting a very cohesive and rubbery structure develops (Woodward and Cotterill 1986, 1987a, 1987b). Although the egg white starts to coagulate at relatively low temperatures (around 60 °C), an effect connected with conalbumin denaturation, gel formation, and structure consolidation requires heating at higher temperatures. The gelation process is completed when the major albumen protein ovalbumin is denatured at 85 °C and becomes involved in the development of the gel network (Paraskevopoulou and others 2000). Extensive covalent bond formation between interacting albumen protein molecules seems to play a dominant role in egg white gelation (van Kleef and others 1978), although the physicochemical properties of the final gel are greatly influenced by the pH and the ionic strength conditions of the system (Woodward 1990, Croguennec and others 2002).

Yolk gelation may be envisaged as a process of yolk particle destabilization resulting from heat denaturation of protein constituent molecules present at the particle surface (Kiosseoglou 2003a, 2003b). Anton and others (2001) reported that the gelation process of yolk is dominated by the protein constituents of the plasma, the livetins and the apolipovitellenins, while the contribution of the granular constituents to the building up of the gel network is less important. According to Kiosseoglou and Paraskevopoulou (2005), intact granules may act as "non-active" fillers of the yolk gel structure that starts to develop as a result of interactions involving the heat-sensitive livetin molecules and is consolidated by interacting apovitellenin constituents from LDL micelles, which begin to denature at 70 °C. Denaturation of the granular protein constituents above 75 °C may not play a significant role in yolk gel structure formation, as long as the granular lipoproteins are entrapped in the granular structure associated with phosvitin. The granular proteins may contribute to the development of the yolk gel network structure only if the granules are dispersed in high ionic strength environments and their protein constituents are liberated.

Disulfide bridges seem to play a key role in yolk gel network formation. As reported by Kiosseoglou (2003b), covalent disulfide bonds between interacting yolk protein molecules could be the result of either oxidation of sulfhydryl groups or sulfhydryl–disulfide reactions, with the reacting groups becoming exposed following heating and molecular unfolding. Research findings (Kiosseoglou and Paraskevopoulou 2005) indicated that both the plasma and the granular protein constituents may interact through intermolecular disulfide bridges

and contribute to the building up of the gel network structure of each fraction.

The presence of yolk emulsified with oil droplets in a gel network structure, resulting from egg protein heat denaturation and interaction, may influence the gel strength depending on the nature of the egg proteins involved in gel formation. In the case of a gel based on egg yolk, protein interaction of the gel network with the oil droplet surface constituents is not possible and the oil droplets act as non-active fillers of the gel network resulting in the weakening of the final gel structure (Anton and others 2001; Kalkani and others 2007). When egg white is incorporated in a yolk-stabilized emulsion and the system is subjected to heat treatment, the egg white proteins of the continuous phase may denature and become involved in interactions with the yolk proteins adsorbed at the oil droplet surface. At a relatively high egg white concentration, the gel network structure that develops as a result of egg white protein interactions in the emulsion continuous phase is strengthened by the simultaneous interactions of the gel network proteins with the oil droplet surface yolk protein constituents, indicating that the oil droplets may function as active filler particles of the egg white protein gel (Kalkani and others 2007).

Egg as a functional ingredient in baking

Incorporation into baked foods of egg or egg fractions in the liquid, dehydrated or frozen form, aims not only at enhancing their nutritional value but also at improving the functional properties of the ingredients to obtain a food with acceptable quality characteristics and prolonged shelf-life. In cookies, biscuits, and pastry, egg may constitute an optional ingredient incorporated to modify certain product characteristics such as texture, flavor, or color. However, egg omission from the recipes of these products should not have any significant adverse effects on their quality. The preparation of certain baked products such as various types of cake is not possible, however, unless egg is incorporated in the food system due to the multifunctional role of the egg constituents during the various stages of the baking process that cannot be effectively performed by any other cake ingredient (flour, sugar, milk or synthetic emulsifiers).

Although there is no doubt about the importance of egg for the preparation of cakes, the mechanism of egg constituent functionality in these systems is far from clear. Depending on the type of cake, either whole egg or only albumen is used. Most of cake types use whole egg, with typical examples being the Madeira and the high-ratio yellow cakes. These cake types contain high proportions of fat that must be dispersed and emulsified during the ingredient mixing stage, a function successfully performed by the yolk lipoproteins, which exhibit outstanding emulsifying properties compared with egg white proteins. Fat-free cake types, on the other hand, contain either whole egg (sponge cake) or egg white (angel food cake), which have to perform only aerating and coagulation/gelation functions during the preparation of the product (Shepherd and Yoell 1976).

The process of cake making can be divided into three main stages: the cake batter preparation, intermediate, and structure development stages. The first stage involves mixing the cake ingredients to obtain an aerated dispersion system, with water constituting the continuous phase in which the fat and flour are dispersed. The air, depending on the cake type and the mode of ingredient incorporation, may be found either within the fat phase of the cake batter or dispersed in the form of small-sized bubbles in the continuous phase of the system. In fat-containing cakes, emulsification of fat should be solely performed by the yolk lipoproteins, due to their ability to rapidly adsorb and rearrange at o/w interfaces, displacing the globular proteins of egg white.

Although there is no doubt about the dominant role of yolk constituents in dispersing the fat and in stabilizing the fat globules in cake batter, the relative importance of the egg fractions – the yolk and the white – in aiding air entrapment and subsequent stabilization of air bubbles against coalescence and/or disproportionation has not currently been clearly established. The presence of yolk is considered detrimental to the foaming properties of egg white. In sponge cakes and in other cake types, however, whole egg is used. The lipovitellenin components seem to assist in aeration and foaming, while the high-density lipovitellin components of the granules inhibit air incorporation but aid in the retention of air whipped into the system by the low-density lipovitellenin and egg white (Kamat and others 1973; Graham and Kamat 1977). According to Shepherd and Yoell (1976), the aerating action of the yolk components could be connected with their ability to become adsorbed at the air bubble surface and increase the elasticity of the surface membrane, especially during the bubble expansion

phase. It is also highly probable that when air bubbles are stabilized by whole egg, the more surface-active yolk lipoproteins may antagonize the albumin proteins, leading eventually to their expulsion from the interface. Such effects were reported for the less surface-active whey proteins (compared to yolk lipoproteins), which were found to dominate the air–water interface when used in a mixture with egg white (Yang and others 2009). In the angel food cake batter system, air inclusion depends solely on the white protein constituents, mainly the globulins and ovalbumin, while the bubbles are stabilized by the thickening effect of ovomucin on the liquid films formed between neighboring bubbles.

The stabilizing effect of egg constituents on both the fat and air dispersions of cake batter continues to operate during the intermediate stage of baking. When the fat melts and folds into oil droplets, the air bubbles move into the water and start to expand as a result of the leavening action of the baking powder releasing CO_2, and the increase in vapor pressure with temperature inside the bubbles. Partial oil globule coalescence may take place as the temperature rises, leading to fat release; the released fats may then form a fat layer covering the surface of the collapsed bubbles of the final cake structure. An appreciable proportion of fat, however, remains dispersed within the coagulated protein and the gelatinized starch of the final cake network structure (Shepherd and Yoell 1976). This suggests that part of the fat remains in the emulsified form, and the surface lipoprotein membrane may become involved in protein–protein interactions with the protein components of the gel network structure and thus modify the mechanical properties of the final product.

As Mizukoshi (1990) reported, the rigidity of cakes increases or decreases depending on the incorporation of either fat or oil, respectively, indicating that the fat or oil globules may act as fillers of the gel network and determine the final product's textural and rheological properties. Sowmya and others (2009) found that replacement of fat with sesame oil results in harder cakes, which may be connected with the reduced final product volume and its more compact structure. On the other hand, Matsakidou and others (2010) reported that substitution of margarine with olive oil resulted in a Madeira-type cake with increased batter density and increased cake volume, structure rigidity, and cohesiveness. These findings indicate that the physical properties of the emulsified fat/oil phase in a cake structure may influence structural and textural characteristics of the product, probably as a result of interactions of the emulsified fat/oil surface proteins with other structural components of the cake matrix. Air bubble expansion, combined with continuous phase viscosity reduction during the intermediate baking process, may impose a significant strain on the foam system, leading to air escape and collapse. Such adverse phenomena are prevented by the high elasticity exhibited by the egg white and yolk protein films at the air bubble surface. In angel food cakes, the high cake volume is connected to the globulin, ovalbumin, and ovomucin fractions. Lysozyme aids in the prevention of cake collapse, an effect attributed to the formation of a ovomucin–lysozyme complex that alters the protein denaturation and aggregation behavior upon heating (Johnson and Zabik 1981a, 1981b). Cakes having a lower volume, however, are obtained when egg white is replaced by whey protein (Arunepanlop and others 1996), something that was also reported by Pernell and others (2002). It seems that proteins other than egg white have a lower ability to prevent collapse of angel food cake structure during the final stage of baking, although they may have satisfactory foaming properties. According to Pernell and others (2002), angel food cake batters containing whey proteins become less elastic than traditional batters containing egg white at baking temperatures from 60 to 85 ℃ and the resulting heat-set gel network structure is not able to

prevent collapse once starch gelatinization begins. Other papers (Berry and others 2009; Yang and Foegeding 2010) indicated that egg white protein expulsion from the bubble surfaces by the more surface-active whey proteins led to a decrease in the elasticity of the surface film, which was then based on adsorbed whey proteins interacting at the bubble surface. As a result, extensive bubble coalescence/disproportionation takes place at very early stages of baking and the original foam structure breaks down, in straight contrast to the foam based on egg white, which maintains its structure through heating to 85 °C, leading to starch gelatinization and structure consolidation, which stabilizes the expanding bubbles.

It seems, therefore, that the process of egg protein coagulation leads to a gel network development above 70 °C. Following egg yolk or white protein denaturation and starch gelatinization, a change at this stage involving extensive bubble coalescence followed by channeling, which allows escape of air and vapor from the cake structure, is crucial to prevent collapse phenomena and to transform the foam into a sponge (Lillford and Judge 1989). The final cake structure is a solid foam exhibiting extensive cell connectivity and having cell walls of high brittleness and relatively low elasticity. This is probably due to the egg proteins in the system, which prevent extensive gluten network formation throughout the cake structure, but only locally produce a composite gel matrix reinforced by gelatinized starch granules that exhibit a crumbly texture.

Interruption of the thiol–disulfide interactions responsible for gluten network development could be the result of interactions between egg protein and gluten protein. Both the egg white and the yolk protein constituents can become involved in disulfide bond bridges when they are denatured above 70 °C (Kiosseoglou 2004). Additionally, when whole egg is incorporated into a cake system, both the egg white and the yolk proteins seem to contribute to structure development, producing a phase-separated gel network structure, with the yolk constituting the continuous phase of the system (Paraskevopoulou and others 2000). The final cake structure, therefore, is a mixed gel network system based on gluten development (Wilderjans and others 2008, 2010), but significantly modulated by the heat-setting ability of the egg proteins, resulting in a product that exhibits higher brittleness and lower elasticity than bread (Davies 1986).

The importance of the involvement of yolk protein constituents in cake structure development was pointed out by Paraskevopoulou and Kiosseoglou (1997), who investigated the textural and physical properties of Madeira-type cakes prepared with yolk protein concentrates (60% protein). Compared with the control sample prepared with spray-dried yolk, the cakes based on yolk protein concentrate exhibited much greater hardness, although their volume, expressed as cross-sectional area, was not significantly affected. This suggested that the cake matrix was reinforced by the yolk protein constituents, which seemed to contribute to cell wall structure development, along with the egg white proteins.

In conclusion, the cake structure development is dictated mainly by the interplay between functional constituents originating from egg and flour and is bound to depend on the amount and the relative ratio of these important cake ingredients. Proteins from egg perform both as emulsifiers and foaming agents right from the beginning of the process of cake preparation and cake batter formation, while their denaturation during the intermediate and mainly during the final baking stage aid in the consolidation of the final cake structure along with gluten structure development and starch gelatinization and amylose release (Figure 13.1). The mechanism of egg protein constituent involvement in cake structure development and its

influence on final product properties, however, require further clarification.
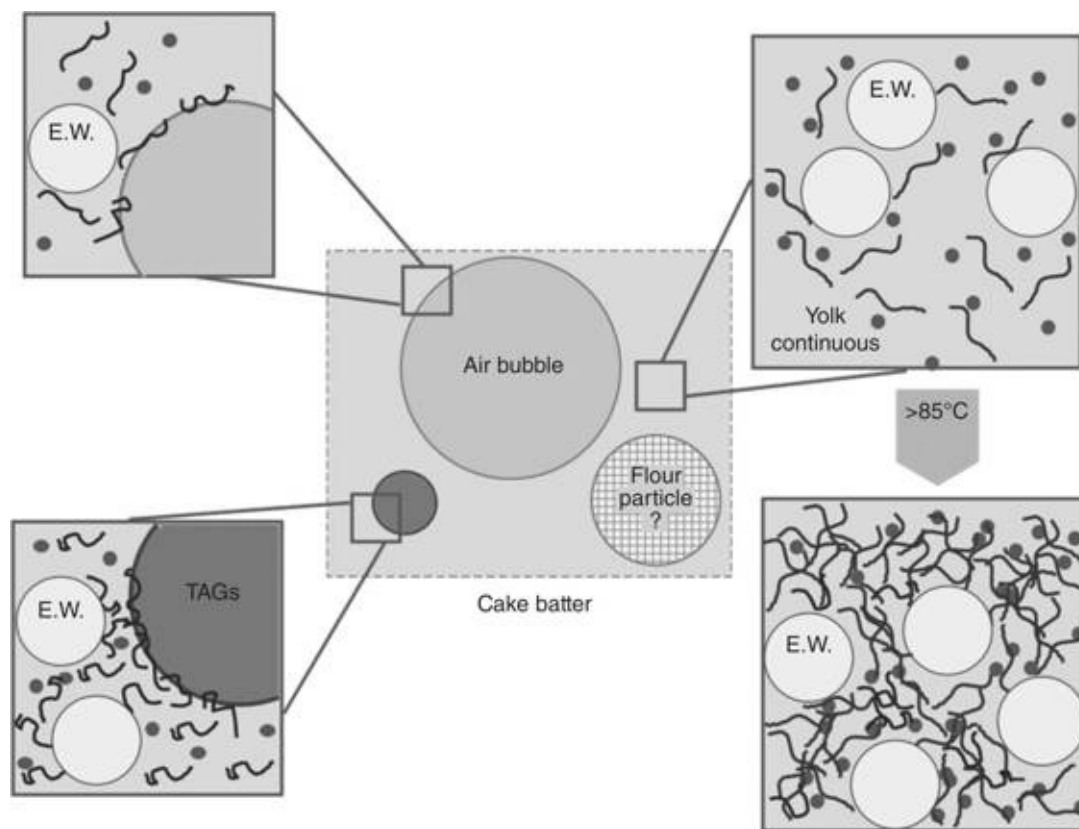
Figure 13.1 Schematic representation of egg functionality in cakes.

Baked products, especially cakes, are systems in which a number of protein constituents, differing both in structure and functionality, interact with each other to produce a phase-separated coagulated protein network (Tolstoguzov 1996) exhibiting the unique structural and textural characteristics of these systems. The investigation of the relationship between phase separation phenomena expected to occur in cake systems and the final product structure, should be based on a thorough understanding of the mechanisms operating when a number of biopolymers of a diverse nature are forced to coexist in the system and interact as a result of heating during the intermediate and the final baking stages.

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14
Dairy Ingredients

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General aspects of milk

Milk is defined as the whole, unadulterated, and unaltered product obtained from the hygienic and regular milking of healthy and well-fed mammal females, without colostrum. The benefits of milk on human nutrition and the need to preserve its quality have led the development of a wide variety of dairy products. Dairy products are obtained by the partial or total elimination of water (milk concentrates and powdered milk), by lactic-acid coagulation of milk proteins (fermented milks), by acid or rennet coagulation of milk proteins and the subsequent separation of whey (acid or rennet cheese), or by the separation of milk components (protein concentrates, cream, lactose). In the food industry, both milk and dairy products have an extensive applicability thanks to their technological properties (emulsifying capacity, foam and gel formation, and so on) and nutritional characteristics. All these characteristics depend directly on their physicochemical composition.

Chemical composition of milk

The main components of milk are water, fat, proteins, and lactose; other components include organic and inorganic salts, minerals, and vitamins. The proximate composition of milk from the main productive species is shown in Table 14.1.

Table 14.1 Approximate composition (%) of milk from the main productive species (Fox 2003). (Adapted from Fox & McSweeney 1998. Reproduced with permission of Springer Science + Business Media).

	Total solids	Fat	Protein	Lactose	Ash
Woman	12.2	3.8	1.0	7.0	0.2
Cow	12.7	3.7	3.4	4.8	0.7
Goat	12.3	4.5	2.9	4.1	0.8
Ewe	19.3	7.4	4.5	4.8	1.0
Mare	11.2	1.9	2.5	6.2	0.5
Reindeer	33.1	16.9	11.5	2.8	–

Milk fat forms fat globules (diameter, 0.1–22 μm) are surrounded by a protein membrane (Fox and McSweeney 1998). These globules are mainly composed of triglycerides (97–98%), but they also contain phospholipids (0.2–1%), sterols (0.2–0.4%) and free fatty acids. The main fatty acids are saturated (65%) and longer than 16 carbons (75%). Production-related factors, such as species or feeding system, modify the quantity and characteristics of the fat, and industrial treatments, particularly heat, have been shown to have a major impact, particularly on the membrane of the fat globules (van Boekel and Walstra 1995).

Apart from fat, milk characteristics are also strongly influenced by its protein content. Of the total protein content of milk, 80% corresponds to caseins and the other 20% to the whey proteins. The caseins are in suspension, forming colloidal particles (super-aggregates) known as casein micelles (50–500 nm) (Fox and McSweeney 1998). There are four main caseins (α_{s2}-, α_{s1}-, β- and κ-), in proportions of 45%, 12%, 34%, and 10%, respectively. These proteins

have a very open structure and low levels of secondary and tertiary structures compared with whey proteins. Caseins are maintained in suspension thanks to the presence of both hydrophilic and lipophilic groups within the same molecule (amphiphilic nature). The hydrophilic amino acid residues are oriented toward the aqueous phase, while the hydrophobic segments of the protein molecules are attached to the fat globules. Casein aggregation occurs when changes develop in the κ-casein structure, due either to enzymatic cleavage of its hairy layers or to acidification to its isoelectric point (pI = 4.6). Those proteins that remain in solution are called whey proteins (Walstra and Jenness 1984), the principal components of which are β-lactoglobulin and α-lactoalbumin (40% and 20%, respectively, of the total whey proteins). They are typically globular, with high levels of secondary and tertiary structures.

All dairy proteins, including caseins and whey proteins, contain active peptides, which are sequences of amino acids produced by protein hydrolysis and which have biological activity (Gobbetti and others 2004). The protein system also includes enzymes. Although enzymes are present in very small quantities, they have a major biological role. In the dairy industry, proteases and lipases are important for their effect on ripened dairy products such as cheese, and their activity is modified (both increased and reduced) by the technological conditions (Grappin and Beuvier 1997).

Apart from fat and proteins, milk contains lactose, a disaccharide formed of galactose and glucose. This sugar is characterized by its low solubility but, once dissolved, it crystallizes with difficulty and forms supersaturated solutions. Furthermore, lactose has low sweetness, though the sweet taste increases as the concentration rises. Lactose is a reducing sugar, meaning that, at high temperatures, it participates in the Maillard reaction, giving rise to browning components (Smith and Campbell 2007). However, lactose is fermented more slowly by bacteria than many other sugars (Modler 1985) and it is not fermented by baker's yeasts.

The minor components of milk include salts and minerals such as phosphates, citrates, chlorides, sulfates, carbonates and bicarbonates, potassium, calcium, and magnesium, as well as approximately 20 other elements such as copper, iron, silicon, zinc, and iodine. Although they are present at concentrations below 1%, they are important in many aspects of milk processing, such as thermal stability, the stability of fat globules after homogenization, thickening of condensed milk, adequate reconstitution of powdered milk, enzymatic coagulation, and curd characteristics. Raw milk also contains vitamins, both fat soluble (A, D, E) and water soluble (B complex), which vary greatly according to the productive species (Raynal-Ljutovac and others 2008). However, the technological processing of milk considerably reduces their content (Fox and McSweeney 1998).

Functional properties of milk

From a physical point of view, milk is an opaque, whitish fluid that comprises three phases: an aqueous phase, which holds certain components in solution, such as lactose, organic and inorganic salts, vitamins, and other small molecules; a dispersed phase formed of caseins; and an emulsion formed by the fat globules. This structure, and especially the protein characteristics, determines the functional behavior of milk.

The functional properties of milk depend mainly on the hydration capacity of its proteins

(which determines the water holding capacity and viscosity) and the surface phenomena (which determine aggregation, emulsifying and foaming capacities). All these properties are defined by the interactions between components and can be modified by the technological processing conditions.

In the presence of water, dry dairy proteins show different viscosity characteristics and hydration capacity and thus different rheological behavior. Whey proteins give low-viscosity solutions as they are highly soluble and have a low water-holding capacity. In contrast, sodium caseinates, which have a high water-holding capacity, produce high-viscosity solutions which are formed by partially solubilized and swollen particles. These properties are modified by the pH, salt concentration, and thermal treatments (Cheftel and Lorient 1982).

The surface activity of dairy proteins, particularly the caseins, is important in many food product applications. Caseins are maintained in suspension in milk thanks to their amphiphilic nature. However, this equilibrium may be disestablished, leading to aggregation processes, such as flocculation, coagulation, and gelling (Cheftel and Lorient 1982). The amphiphilic nature of the proteins also makes stabilization of emulsions and foams possible. Factors affecting emulsion stability include the size and charge of the particles in the dispersed phase, interfacial tension, protein diffusion, and flexibility of the protein molecule (Fox and Mulvihill 1982). On comparison of the different types of protein, the sodium caseinates show the best emulsifying capacity. Denaturalization and thermal or hydrolytic treatments of milk increase the foaming capacity of dairy proteins, particularly of the whey proteins (Paquet and others 1978).

Nutritional characteristics of milk

Milk is considered to be a beverage with health benefits and the consumption of dairy products is associated with overall diet quality. Milk provides an easily accessible matrix, rich in a large variety of essential nutrients including minerals, vitamins, and easily digestible proteins with balanced amino acid profiles (Steijns 2008). Furthermore, milk consumption has demonstrated health benefits: the maintenance of strong bones (Bonjour 2005); reduced risk of hypertension or cancer and weight control (Huth and others 2006); and regulation of the blood pressure (López-Fandiño and others 2006). The beneficial effects of the different components of milk have favored the development of functional dairy products, the most common being those with probiotic bacteria, frequently enriched with prebiotic carbohydrates (Saxelin and others 2000).

Despite of the beneficial effects of milk, the content of saturated fatty acids, a risk factor for coronary heart disease (CHD), has decreased its popularity as a health product. However, there is no strong evidence that dairy products increase the risk of CHD (Tholstrup 2006). Another controversial health aspect of milk is the presence of *trans* fatty acids, as in other ruminant products. However, Mozaffarian and others (2006) indicated that the public health implications of consuming natural *trans* fats are relatively limited.

In addition to these inconveniences, milk is associated with allergies and intolerances. Allergy to cow's milk proteins is one of the most common food allergies in children. The symptoms of this hypersensitivity vary considerably and include cutaneous, intestinal, and respiratory symptoms and even anaphylactic reactions (Taylor 1986). Cow's milk contains more than 20 proteins that can cause allergic reactions (Docena and others 1996), but most

studies have shown that the caseins and β-lactoglobulin are the principal allergens (Cocco and others 2003). Apart from allergies, a deficiency of certain enzymes may give rise to intolerance to specific milk components. Lactose intolerance occurs due to decreased intestinal lactase activity (Friedl 1981), causing diarrhea, flatulence, bloating, and abdominal pain. Another much less frequent intolerance (1 in 50 000 births) is galactosemia, which is due to a deficiency of the enzyme galactose-1-phosphate uridylyltransferase (Berry 2012).

The chemical, physical and organoleptic properties of milk make it a very interesting food from the nutritional and technological points of view. It is necessary to apply certain treatments to make milk adequate for consumption, however, whether as liquid milk or as base for dairy products. The main processes used to obtain dairy products are summarized in Table 14.2.

Table 14.2 Summary of the dairy products obtained by milk processing

Process	Dairy product
Skimming	Cream
	Non-fat milk
Concentration	Evaporated milk
	Condensed milk
Drying	Powder milk
Fermentation	Fermented milks
Coagulation	Cheese
	Curd
	Whey

Liquid milk and milk concentrates

Liquid milk

Raw milk is a sterile white secretion, but it is rapidly contaminated by microorganisms present in the udder duct and in the farm environment. To make milk adequate for consumption, thermal treatments such as pasteurization (LTLT: 63 °C, 30 min; or HTST: 72 °C, 15 s) or sterilization (discontinuous: 114–120 °C, 20–30 min; or UHT: 135 °C for a few seconds) are applied.

Sterilization processes increase shelf-life compared to pasteurization, but induce changes in milk, such as the denaturation of whey proteins and their complexation with caseins (Mulvihill and Donovan 1987) as well as a fall in the non-casein nitrogen content and in micelle hydration (Gaucher and others 2008), which mainly modify renneting properties, digestibility, and nutritional value. In addition, lactose participates in the Maillard reaction giving rise to colored compounds that are responsible for a caramel flavor and taste.

Nowadays, UHT technology is the most widely used process to prepare liquid milk for consumption. UHT technology is applied in combination with standardization (adjustment of the fat content by the addition or removal of cream) and fat homogenization (reduction of fat globule size to avoid aggregation and cream separation). Depending on the final fat content, milk is classified as whole fat, semi-skimmed, or skimmed (Table 14.3).

Table 14.3 Nutritional composition (approximate) of dairy products[a] (USDA 2011)

	Whole liquid milk	Evaporated milk	Condensed milk	Non-fat powder milk	Yoghurt	Half-half cream	Gruyere cheese	
Water (g)	87.69	74.04	27.16	3.16	87.90	80.57	33.19	9
Energy (kcal)	64	135	321	362	61	130	413	2
Protein (g)	3.28	6.81	7.91	36.16	3.47	2.96	29.81	0
Total lipid (g)	3.66	7.56	8.70	0.77	3.25	11.50	32.34	0
Carbohydrate, by difference (g)	4.65	10.04	54.40	51.98	4.66	4.30	0.36	5
Fibre, total dietary	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
Sugars (g)	4.65	10.04	54.40	51.98	4.66	0.16	0.36	5
Minerals								
Calcium, Ca (mg)	119	261	284	1257	121	105	1011	1
Iron, Fe (mg)	0.05	0.19	0.19	0.32	0.05	0.07	0.17	0
Magnesium, Mg (mg)	13	24	26	110	12	10	36	1

Phosphorus, P (mg)	93	203	253	968	95	95	605	7
Potassium, K (mg)	151	303	371	1794	155	130	81	1
Sodium, Na (mg)	49	106	127	535	46	41	336	4
Zinc, Zn (mg)	0.38	0.77	0.94	4.08	0.59	0.51	3.90	0
Vitamins								
Vitamin C (mg)	1.5	1.9	2.6	6.8	0.5	0.9	0.0	0
Thiamine (mg)	0.038	0.047	0.090	0.415	0.029	0.035	0.060	0
Riboflavin (mg)	0.161	0.316	0.416	1.550	0.142	0.149	0.279	0
Niacin (mg)	0.084	0.194	0.210	0.951	0.075	0.078	0.106	0
Vitamin B_6 (mg)	0.042	0.050	0.051	0.361	0.032	0.039	0.081	0
Folate (µgDFE)[b]	5	8	11	50	7	3	10	2
Vitamin B_{12} (µg)	0.36	0.16	0.44	4.03	0.37	0.33	1.60	0
Vitamin A (IU)[c]	138	239	267	22	99	354	948	7
Vitamin E (α-tocopherol) (mg)	0.0	0.16	0.16	0.00	0.06	0.33	0.28	0
Vitamin D (IU)[c]	0.0	6	6	0	2	8	24	0
Vitamin K (phylloquinone) (µg)	0.0	0.6	0.6	0.1	0.2	1.3	2.7	0
Fats								
Saturated fatty acids (g)	2.278	4.591	5.486	0.499	2.096	7.158	18.913	0
Monounsaturated fatty acids (g)	1.057	2.335	2.427	0.201	0.893	3.321	10.043	0
Polyunsaturated fatty acids (g)	0.136	0.245	0.337	0.030	0.092	0.427	1.733	0
Cholesterol (mg)	14	29	34	20	13	37	110	1

[a] Values per 100 g of product.

[b] Dietary folate equivalents.

[c] International units.

Milk concentrates

Milk concentrates (evaporated and condensed milks) are obtained by reduction of the water content of liquid milk. These products offer specific characteristics when used as ingredients (viscosity, gelling and foaming capacity, texture, and flavor). Milk concentrates are usually used as ingredient in the confectionery industry and as filling and topping. Their composition

is indicated in Table 14.3.

Evaporated or unsweetened milk concentrate is obtained by the partial removal of water by evaporation from liquid milk that has previously been sterilized and homogenized. Viscosity increases due to whey protein denaturalization as the thermal conditions (time and temperature) increase (Velez-Ruiz and Barbosa-Cánovas 1998). Evaporation also determines the concentration of products obtained during the Maillard reaction. To obtain condensed or sweetened milk concentrate, a solution of refined sugar is added to the concentrate after the partial evaporation of water (Webb and Hufnagel 1948). The high sugar content inhibits the growth of bacteria and moulds despite the fact that the concentrate is not sterilized.

Powdered milk

Powdered milk is obtained by the total elimination of water from liquid milk. The elimination of water increases the shelf-life, facilitates handling, and decreases storage and transport costs. Skimmed or non-fat powdered milk (NFPM) is the most widely used dairy ingredient because of its functional characteristics, lower cost, and longer shelf-life compared with other dairy ingredients. This product is formed mainly of proteins as the water and fat have been removed (see Table 14.3).

The process for obtaining powdered milk is initially similar to that for evaporated milk, but this is then followed by a (thermal) drying process. Today, most powder is spray-dried, although limited quantities are foam dried or roller dried. The conditions of this treatment determine the characteristics of the powdered milk (solubility, dispersability, flavor, taste) and, therefore, its applicability. A number of changes occur in milk during heating, such as whey protein denaturation, complexation of denatured whey proteins with the casein micelle, transfer of soluble calcium and phosphate to the colloidal phase, destruction of bacteria, and inactivation of enzymes (Singh and Newstead 1992). The intensity of the thermal treatment determines three different categories depending on the quantity of whey proteins remaining intact after the treatment (measured using the whey protein nitrogen index): up to 1.50 mg/g intact whey proteins indicates intense thermal treatment; from 1.51 to 5.99 mg/g indicates an intermediate treatment, and above 6.00 mg/g indicates mild thermal treatment. Powdered milk produced using intense treatments (82 °C for 30 min, for example) is difficult to disperse due to limited solubility, whereas mild thermal treatments are ideal for dairy ingredients and drinks production.

Cream

Cream is the milk fat. Fat separation, performed by centrifugation in a skimmer, allows a fat emulsion in water to be obtained. After skimming and adjustment of the fat content, the cream is pasteurized and subsequently undergoes a maturation process at low temperature to make the fat crystallize. The composition of half-half cream is shown in Table 14.3. Before storage, cream may undergo certain treatments to increase the shelf-life (pasteurization, sterilization, freezing, drying) or may be used to prepare other products (whipped cream, butter, anhydrous fat).

Whipped cream is widely used as a filling in confectionery and bakery products. During beating, air is incorporated as bubbles which increase in number with continuous beating (Precht 1988). Finally, the fat globules in contact with the air bubbles are irreversibly adsorbed onto the air–water interface, stabilizing the foam of the whipped cream. Continuous and vigorous agitation of cream (oil-in-water emulsion – O/W) produces butter (water-in-oil emulsion – W/O). The remaining liquid is called buttermilk. Anhydrous milk fat is obtained when butter is melted and the butter oil formed is separated (elimination of water and proteins).

Yoghurt and fermented milks

Milk fermentation is one of the most ancient conservation processes. The increase in the shelf-life is due to the fall in the pH caused by the transformation of lactose into lactic acid by lactic acid bacteria. Yoghurt is the most popular fermented milk product worldwide. Other examples include sour milk, cultured buttermilk, and sour cream. There are other products in which the fermentation process is caused by a combination of lactic acid bacteria and yeasts, such as kefir, or lactic acid bacteria and moulds, such as Viili (Tamime and Robinson 1999). The consumption of fermented milk products has increased dramatically over the past few decades (IDF 2009) as a result of their presumed beneficial effects on health (Chandan 1999). Nevertheless, their use as ingredients in the food industry is minimal.

Cheese and derivates

Cheese

Basically, the preparation of natural cheese consists of the coagulation of milk and drainage of the whey produced. The coagulation of milk occurs either by the enzymatic action of animal proteases (such as chymosin from calf stomach), vegetal proteases (for example, from *Cynara cardunculus*), microbial proteases (for example, from *Rhizomucor miehei*), or through the isoelectric precipitation of caseins by the action of lactic acid bacterial cultures or the direct addition of acid. The simultaneous use of enzymes and acid in the coagulation process is also common. The type of coagulant used will determine the characteristics of the cheese (Broome and Limsowtin 1998). The coagulation conditions (Johnston and others 1994) and the subsequent processing, such as drainage (Holmes and others 1977), compression (Sheehan and Guinee 2004) and salting (Pastorino and others 2003), and the storage conditions also have a marked effect on the yield, composition, and quality of the cheese. Recently, ultrafiltration has been applied to milk to retain fat and whey proteins and thus improve cheese yield. But it is the variation in the processing conditions in cheese production that enables such a wide variety of cheeses to be obtained. As an example, the composition of gruyere cheese is shown in Table 14.3.

Processed cheeses are prepared by adding melting salts to mixtures of grated ripened cheeses with different ripening times. Likewise, cheese analogues can be prepared either from dairy ingredients (cream and dairy proteins) or from non-dairy ingredients (vegetal oil and proteins). In contrast to natural cheese, processed cheese and cheese analogues have wide applications as ingredients in other food products as they are designed according to industry requirements (fluidity, extensibility, melting point) and consumer demands (fat content, type of fatty acids, cholesterol content). Furthermore, they do not have the slight variations in composition and quality that natural cheeses have, and their price is much lower.

Whey

Whey is the aqueous solution obtained after milk coagulation. Its composition, organoleptic characteristics, and functionality thus depend on the type of cheese obtained (rennet or acid coagulation). Whey has the advantage of low cost compared to other dairy ingredients as it is a by-product from the cheese industry. Liquid whey is used to create different products, such as powder whey, sweet and acid whey (see Table 14.3), whey with reduced lactose or mineral content, and whey protein concentrates and isolates, which have much greater technological applicability than whey itself. The process to obtain powdered whey is similar to that for NFPM (Chandan 1997). Whey with reduced lactose content (< 60%) is obtained by crystallization of most of the lactose. Whey can be also demineralized, or it can be acidified to make whey protein precipitate.

Protein concentrates

Dairy protein concentrates can be caseins or whey proteins. Casein products are obtained by the acidification (lactic, hydrochloric or sulfuric acids) or enzymatic hydrolysis (rennet, for

example) of skimmed milk. Subsequently, wet casein precipitate is processed by draining the whey and washing, pressing, milling, drying, grinding, sieving, and bagging the curd. The caseinates are produced by the transformation of curd or reconstituted powdered casein into sodium, potassium, ammonia or calcium caseinate by neutralization to pH 6.8–7.5. Caseinates have little similarity to the casein micelles of milk as the colloidal structure has been transformed into aggregates. Casein and caseinate properties are influenced to a great extent by the production method and by the properties of the food matrix into which they are incorporated (Trejo and Harte 2010). Caseins and caseinates are usually used in food product applications requiring solubility, heat stability, and surface-active properties (emulsifying, foaming) (Morr 1979).

Whey proteins concentrates are obtained by the elimination of minerals and lactose from whey followed by concentration and drying. These products are well known for their versatile functional properties in food products. However, these properties are often impaired by inevitable heat treatments during processing (Wit 1990) and by the ionic environment (Hollar and Parris 1995). Whey protein concentrates are classified into whey protein concentrates (35–80% protein) and whey protein isolates (> 90% protein). The difference in protein composition between the various types of whey will be reflected in their applications. The whey protein concentrates with 35% protein are commonly used as skimmed milk substitutes. Whey protein concentrates with a protein percentage between 50 and 80% produce suspensions in a wide pH range and they can be used as an economic substitute for egg white (Chandan, 1997). Whey protein isolate excels in its gelling and foaming properties because of its high protein content. Whey protein and casein composite blends are also used in the food industry (Britten and Giroux 1991).

Lactose

The most widely used method to obtain lactose is by crystallization either from concentrated whey or from concentrated permeate of whey ultrafiltration. Crystallization consists of a two-step process involving nucleation and growth of the nucleus to a macro-size (Nickerson, 1974). After crystallization, crystals are separated by centrifugation and are then dried, milled, sifted, and packed (Holsinger 1997). The low sweetness of lactose limits its use as a sweetener in the food industry. However, it is used as a sticking agent because it improves the functionality of shortenings in the confectionery industry, as an anticaking agent at a high relative humidity, and as a reducing sugar if Maillard browning is required. Additionally, it may be used as a diluent for food flavors or pigments.

Role of dairy ingredients in bakery products

The use of dairy ingredients in bakery products is common practice in many countries. The addition of milk or its derivates to bakery products modifies their internal structure, enhances certain flavors and changes crust color (Stahel 1983; Cocup and Sanderson 1987; Mannie and Asp 1999). The first studies on the use of dairy ingredients in bakery date back the first half of the 20th century. Those studies emphasized the nutritional improvement obtained by the incorporation of milk into bakery products, in particular the quality of proteins, vitamins, and minerals (Carlson and others 1946; Henry and others 1946; Riggs and others 1946). However, there has recently been an opposite trend in many countries due to the increase in the number of individuals who are lactose-intolerant or allergic to milk proteins or who reject milk consumption for various reasons. Thus, removing dairy products from bakery formulations could increase the market share of those products. This fact is especially noticeable in the preparation of gluten-free products, because gluten intolerance is often associated with other intolerances, such as lactose intolerance.

In Western countries, the ready availability and low cost of cow's milk make it the most extensively used milk in bakery products. However, for cultural reasons or availability, other varieties of milk are used (ewe, goat) in some countries, especially in artisan production. For dairy products, NFPM is the most extensively used ingredient because it has a long shelf-life product with a low water and fat content and good organoleptic and nutritional characteristics. In some cases whey powder is also used, particularly for its low cost, even though its nutritional and organoleptic characteristics are poorer than those of NFPM. Casein and whey protein concentrates are also extensively used. The use of liquid milk (pasteurized or sterilized) in industry is limited to certain artisan productions, as it leads to unnecessary transport and storage costs (it is mainly transported as stored water) and requires a high turnover due to its very short shelf-life. The use of full fat dry milk is not common because of its high price and its relatively short shelf-life due to fat rancidity. When the incorporation of dairy fat is required, it is more common to use NFPM combined with cream, butter or anhydrous fat.

When analyzing the effect of the addition of dairy ingredients to bakery processes and final products, it is necessary to take into account the composition of the ingredients and the processes that they have undergone. For instance, dairy ingredients rich in fat will have an influence on bakery products in the same way as other similar fats, and dairy ingredients with lactose, a reducing sugar, will modify the crust color due to Maillard reactions.

Dough and bread

Dough and bread characteristics are modified by adding dairy ingredients. When NFPM is added, it is necessary to consider certain aspects such as the percentage added (usually around 5%), the quality of the milk, and the changes that occur in the milk during the production process. In general, the addition of NFPM increases water absorption, approximately to the same extent as the percentage of NFPM incorporated (Stamberg 1946). Mixing time should be also increased, though the consistency of the dough increases to some extent during fermentation due to hydration of the NFPM. In general, mixing of the NFPM with the flour before mixing the dough is recommended to prevent the formation of lumps.

No advantages are observed, however, when NFPM and water are mixed before their incorporation into the dough (Pyler and Gorton 2008). Exceeding the optimum mixing time is not advisable either, as tolerance to over-mixing is reduced (Kenny and others 2000). Furthermore, the addition of NFPM usually needs a higher temperature at the end of mixing and longer resting times before forming, so that fermentation processes improve dough machinability. It can be also helpful if flour strength is increased or oxidizers are used. In addition, the incorporation of NFPM improves the tolerance to excess oxidizer; in fact breads with increased volume and improved alveoli and texture were obtained in breads with potassium bromate (Ling and others 1976, 1977).

The influence of NFPM on dough rheology depends on dough composition, and particularly on the dairy protein–gluten interaction. Kenny and others (2000) studied the influence of various dairy ingredients on dough characteristics and observed that the addition of dairy proteins (4%) increased farinographic stability. They also observed that sodium caseinate increased absorption but that whey protein concentrate slightly reduced it, and in both cases there was an initial fall in resistance to extension measured with an extensograph, but this increased noticeably if the resting time was increased. The different treatments applied to these proteins also affected the rheological properties. The drying process, with high or low levels of protein denaturalization, can affect the properties of dairy ingredients used in bread making.

In the sponge-and-dough process, NFPM is usually added in the dough step, although it can be also added totally or partially in the sponge step when using flours with a low protein content or low strength, with excessive amylase activity, or with low fermentation tolerance (Pyler and Gorton 2008), in order to compensate these effects.

NFPM addition reduces fermentation capacity by increasing dough pH, due to its buffer effect, moving away from the optimum pH for amylase to transform starch into fermentable sugars (Skovholt and Bailey 1932). It is therefore advisable to slightly increase fermentation times or increase the yeast quantity to 0.2–0.4% (Dubois and Dreese 1984). As a positive effect, NFPM increases dough tolerance to over-fermentation, avoiding the dough falling when excessive fermentation occurs, thus improving the regularity of productions. It is usually advisable to reduce the humidity of the fermentation chambers compared to processes without NFPM (Pyler and Gorton 2008).

The addition of NFPM also improves bread taste. Doerry (1989) demonstrated that the addition of 4–6% NFPM makes it possible to obtain breads by the no-time dough system, similar to those obtained by the sponge-and-dough system. The effect of the addition of dairy ingredients on volume increase during fermentation also depends on the protein characteristics. Kenny and others (2000) observed that sodium caseinate improves dough development but that whey proteins reduce it. The effect of sodium caseinate on the organoleptic properties of breads (flavor, odor and texture) was also better than that of whey proteins. The negative effect of whey proteins is caused by the weakening effect on the gluten matrix; this can be eliminated by previous thermal treatment (Kenny and others 2001).

Some authors state that it is inadvisable to add NFPM in continuous mixing systems because this produces bread with a low volume and poor alveoli and texture, and dough with limited tolerance to the fermentation and baking process (Swortfiguer 1962; Doty and McCurrie 1964). The collapse of dough in these phases could be minimized by the addition of emulsifiers such as SSL or DATEM.

Lactose from NFPM is a sugar that cannot be fermented by baking yeasts, and it therefore remains in the dough after fermentation. During baking this sugar takes part in Maillard reactions and favors crust browning. Thus, if baking time is only determined by the crust color, breads with NFPM may be under-baked compared to breads without NFPM. Dubois and Dreese (1984) proposed reducing the baking temperature and increasing the baking time when higher percentages of NFPM were added. It is also important to take into account that the final color will depend on the kind of sugar involved in the Maillard reactions; lactose can produce a reddish color compared to traditional breads. Dubois and Dreese (1984) also observed that breads with NFPM had a longer shelf-life due to a reduction in staling phenomena. This result indicates that NFPM minimizes starch retrogradation. Furthermore, the addition of NFPM improves bread taste, a particularly positive factor in health bread with a low salt content, which is usually tasteless.

As whey has a higher lactose content than NFPM, it has a greater effect on the crust color of breads, cakes, and biscuits than NFPM. Commercially, it is possible to find whey protein isolates with low lactose content, useful for the preparation of products with high protein and low carbohydrate contents and to reduce the fat content in certain breads. As commented earlier, whey proteins interact with gluten in a different way than caseins, producing softer doughs, which could affect dough handling. Whey proteins have good emulsifying properties and will thus contribute to the correct distribution of fat in the dough, resulting in products with better alveoli characteristics and volume (Chandan 2011).

Studies on the inclusion of whey in bread making go back to the 1950s (Larson and others 1952). It has been observed that whey proteins that have not received thermal treatment have a depressant effect on loaf volume (Gordon and others 1953; Volpe and Zabik 1975). The dough softening and volume reduction caused by whey can be reduced by previous thermal or high pressure whey treatments (Erdogdu-Arnoczky and others 1996; Kadharmestan and others 1998). Apart from protein and mineral enrichment, some authors state that the addition of whey decreases bread staling (Yousif and others 1998) and increases the sensorial score (Bilgin and others 2006). Whey may also slow down the fermentation process, and an increase in the quantity of yeast or in the fermentation temperatures has been proposed to counteract this (Divya and Rao 2010). The recommended whey level is not usually higher than 6% in fermented products, 10% in biscuits and pies, and 20% in cakes. As with whey, sodium caseinate reduces bread volume but this effect cannot be reverted by thermal treatment (Erdogdu-Arnoczky and others 1996).

The use of dairy proteins (casein and whey proteins) can also improve the characteristics of the breads prepared with frozen doughs as the size of the crystals formed during freezing is reduced and the texture, the specific volume, and moisture retention are improved in the final bread (Shon and others 2009). Asghar and others (2009) have proposed the use of thermally treated whey proteins to improve the rheology of this kind of dough, achieving good results.

In the case of gluten-free breads, the raw material used is usually maize starch mixed with potato and rice starches. In this case it may be interesting to increase the protein content of the formula in order to improve the nutritional quality of the product. Soya flour or soya protein isolate are usually used, but powdered milk and milk protein isolate could be interesting alternatives and their addition could produce breads with adequate organoleptic characteristics (Gallagher and others 2003a; Sanchez and others 2004). Moore and others

(2004) demonstrated that the use of NFPM reduced the changes in bread texture over time – one of the main problems with this type of bread – and improved bread keeping quality by the formation of gluten-like structures. Gallagher and others (2003b) observed that different dairy derivatives had different effects on bread volume and hardness; those derivatives that contained sodium caseinate and NFPM had the most favorable effect, and those with demineralized whey the least favorable. Nunes and others (2009) observed that the incorporation of whey proteins into gluten-free breads increased bread volume and decreased hardness over time, but that the addition of sodium caseinate had the opposite effect. The type of protein is therefore one of the most important factors in the choice of ingredients. The use of a mesoscopically structured whey protein particle system, obtained from whey protein, locust bean gum, and glucono-delta-lactone, has also been proposed in order to imitate the action of gluten (van Riemsdijk and others 2011). As commented earlier, however, it should noted that coeliac disease may be associated with other food allergies, and many manufacturers therefore prefer to eliminate dairy ingredients from the formula; in addition, these ingredients are of animal origin and the products are thus rejected by vegans.

Commercially, products can also be found that are elaborated from whey with soya derivates, caseinates, maize flour, and mineral salts, and occasionally include dry egg, which aim to imitate or substitute NFPM at lower cost. These products are not usually added directly to the dough, but spray dried onto the product to increase the brightness of the final product. In other cases, a lactose or glucose solution may achieve a similar effect but at a lower cost. It is also possible to use purified lactose, although this is not typically used in bakery products.

In some countries where water is scarce, the use of milk permeate, a by-product obtained from the ultrafiltration of milk during the production of cheese, has been proposed. This by-product, which has 5% solids (90% lactose and an absence of caseins and β-lactoglobulin), may be used to substitute water in bread making without noticeably altering the farinographic characteristics of the dough or the final quality of the bread, though it does improve the tolerance to over-mixing and raises the gelatinization temperature (Al-Eid and others 1999).

Gelinas and Lachance (1995) have proposed the use of fermented dairy ingredients to boost bread flavor or as sourdough bases. These products are obtained from the fermentation of a mixture of milk and whey, with or without the addition of wheat flours, using different cultures, mainly *Lactobacillus* spp. Breads with these ingredients have a higher lactic acid, ethanol, and diacetyl content, and a more intense and pleasant flavor. However, note that the addition of fermented dairy ingredients reduces the peak time, dough mixing stability, and bread specific volume and increases bread firmness (Gelinas and others 1995). On the other hand, yoghurts have low lactose levels and they do not therefore contribute to crust browning to the same extent as other dairy ingredients.

Batters and cakes

For layer cakes, the addition of NFPM increases crust color due to the participation of lactose in the Maillard reactions and improves structural strength (Pearce and others 1984). The caramelization of lactose also contributes to the final flavor and taste of the products. In some preparations, such as high-ratio cakes, dairy proteins can also help to improve air incorporation into the batter, thanks to their emulsifying properties, producing cakes with a high volume, fine alveoli, and a high structural strength. Whey, rich in proteins, can also

fulfill this function. Furthermore, whey proteins denaturalize during baking and show good water-holding capacity in the final product, thus enabling moist and tender products to be obtained. These characteristics will depend on the type of protein and thus on the type of dairy ingredient used. Hanning and Degoumois (1952) observed that the addition of 15% whey improved the volume, texture, and taste of yellow cakes. Specifically, texture was softer, more tender, and moister, and was maintained for longer. However this effect may change depending on the formulation and the type of cake. Mohamed and Hamid (1998) observed that while NFPM improved the texture and volume of rice cakes, whey reduced them. The presence of whey also promoted crust browning due to the lactose and amino acid content, which participate in Maillard reactions. In any case, the addition of milk or dairy ingredients modifies the solids–liquid equilibrium in batters, and requires the reformulation of products according principally to the quantity of water provided by the dairy ingredient and its composition.

Whey protein concentrate and isolate, due to their emulsifying properties, may also be used as an egg substitute in the preparation of angel food cakes. Whey protein isolate is actually one of the most efficient egg substitutes (Jyotsna and others 2007; Abu-Ghoush and others 2010). In this case, the objective is to cut costs or to remove egg from formulations aimed at ovoprotein-allergic individuals. However the properties of whey proteins are poorer than those of egg white proteins. Pernell and others (2002) observed that angel food cakes prepared with whey proteins tended to collapse when starch gelatinization started during baking. This phenomenon could be minimized by the thermal treatment of proteins or by the addition of xanthan gum, but the volume obtained with ovoprotein was never achieved. In fact, xanthan gum improves the overrun of foams prepared with whey protein isolate and their stability (Mott and others 1999), producing angel food cakes similar to those obtained with egg white proteins in appearance, texture, and sensory properties (Arunepanlop and others 1996). Another way to improve the quality of angel food cake with substitutions of 25% of liquid egg white by whey protein isolate consists of modifying the pressure conditions during baking to prevent overexpansion and collapse (Morr and others 2003). It has also been observed that the interaction between whey proteins and sucrose (a basic ingredient in these preparations) is different from the interaction between egg white proteins and sucrose. In fact, the inclusion of sucrose into the foams prepared with egg white improved their stability by increasing interfacial elasticity, whereas it had no effect on the stability of preparations with whey proteins or even reduced interfacial elasticity (Berry and others 2009). Furthermore, the addition of sucrose does not reduce the low stability of foams prepared with whey proteins, during baking (Yang and Foegeding 2010).

In some countries, fermented dairy products such as yoghurts are typically used in cake and muffin making to improve taste and flavor. The acidity of these products also boosts the action of the baking powder. In general, lactic acid releases hydrogen ions rapidly during the baking process and allows the formation of CO_2 in the first stages of baking. However, it may be necessary to modify the type of baking powder used if these kinds of products are added.

Biscuits

For biscuits, NFPM is usually used to improve taste, texture, and color by the Maillard and caramelization reactions in which lactose is involved. NFPM is an expensive ingredient, particularly in low-cost biscuits, and it is therefore usually substituted by whey, certain

sugars, and artificial flours. Parate and others (2011) found that it was possible to add whey protein concentrate to cookies obtaining the optimum sensory score with 25% (substitution of wheat flour), although the diameter was decreased and the thickness was increased. Gallagher and others (2005) observed different effects depending on the protein added. Whey proteins increased the hardness of short dough biscuits proportionately to the quantity added, and increased crust browning, whereas the addition of caseinate gave rise to a relaxation of batters during baking, producing more elongated biscuits. The inclusion of whey protein concentrate also affects batter rheology by decreasing the consistency and increasing the cohesiveness, which is important in the industrial process and reduces stress fractures of biscuits (Conforti and Lupano 2004). For biscuits, NFPM does not usually dissolve well, leading to the formation of lumps; in the cooked product these lumps become dark stains or spots. To avoid this, the NFPM should be hydrated with cold water before its incorporation into the mixer, or it should be added during the premixing stages, though this will depend on the type of batter to be prepared.

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15
Enzymes

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Introduction

A variety of products such as leavened and unleavened breads, pasta, cookies, and breakfast cereals are prepared using wheat. Such a wide variety of food products are prepared only with wheat because of its ability to form viscoelastic dough.

Generally, additives are used in wheat flour for the preparation of various wheat-based products to obtain a better quality product. Dough improvers like oxidizing agents, reducing agents, bleaching agents, emulsifying agents, and surface active agents are added to improve the functionality of flour components to obtain the desired quality product. Oxidizing agents like bromates, ascorbic acid, and azodicarbonamide are added to the flour to improve the dough strength, which yields bread with an improved quality. Disulfide (-S-S-) bond breaking agents like l-cysteine and reduced glutathione are added to mellow strong doughs for the preparation of cookies. These reducing agents decrease the dough mixing, proofing, and fermentation times and improve dough homogeneity to yield a more uniform quality product. Potassium bromate has been used as a dough strengthening agent for decades, but due to its carcinogenic property, use of this oxidizing agent is being avoided (Panozzo and others 1994; Oloyede and Sunmonu 2009). Food industries currently prefer to use enzymes as an alternative to chemical improvers. They are either derived from plants, animals or microorganisms and therefore they are natural and non-toxic. In addition to quality improvement, enzymes were reported to improve the nutraceutical properties of foods (Zheng and others 2009; Ahmed and others 2010; Hemalatha and others 2012). Initially, in this chapter, the basic properties of enzymes that are relevant to their use as baking ingredients are briefly discussed.

Chemistry of enzymes

Enzymes are biological catalysts. Enzyme catalyzed reactions usually take place under relatively mild conditions as compared to the corresponding chemical reactions. They are very specific to the reaction they catalyze. The specificity to the type of substrate has become the basis for enzyme classification and nomenclature. Many enzymes are named by adding the suffix "ase" to the name of their substrate. For example, protease is the enzyme that catalyzes the hydrolysis of proteins, and polyphenol oxidase (PPO) is the enzyme that oxidizes its substrate, polyphenol (e.g. catechol) into quinines. However, some enzymes described in the past – such as trypsin, pepsin, papain, and so on – have names that do not contain their substrate names (Nelson and Cox 2003).

Properties of enzymes

Most enzymes are proteins with the exception of RNA molecules (ribozymes). They are mostly soluble in water or dilute salt solutions. But they are precipitated by higher concentrations of salts like ammonium sulfate, or high concentrations (70–80%) of organic solvents like alcohols or acetone. Enzymes are globular in nature with different sizes. They exist in monomeric or oligomeric forms. Most enzymes have molecular weights ranging from 12 000 to more than one million, but most cellular enzymes have molecular weights between 30 000 and 100 000. In addition to the protein part, many enzymes contain a non-protein chemical component called a co-factor. These non-protein units may be either inorganic ions such as Zn^{2+}, Fe^{2+}, and so on, or complex organic molecules like NAD^+ and FAD (co-enzymes).

Only a small portion of the enzyme molecule is involved in the enzyme–substrate reaction. This portion is called active site and is the region which contains amino acid residues that directly bind substrate and participates in a chemical reaction (making and breaking chemical bonds). The amino acid residues are called catalytic groups. The substrate has high affinity to bind to the enzyme, thus it readily forms an enzyme–substrate complex (ES) with the enzyme. The enzyme in this complex helps the substrate to overcome the Gibbs free energy of activation by decreasing it. This complex formation facilitates the chemical reaction that transforms substrate to product. As the product formed has a very low affinity it easily dissociates from the ES complex (Equation 15.1).

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [ES] \xrightarrow{k_3} E + P \qquad (15.1)$$
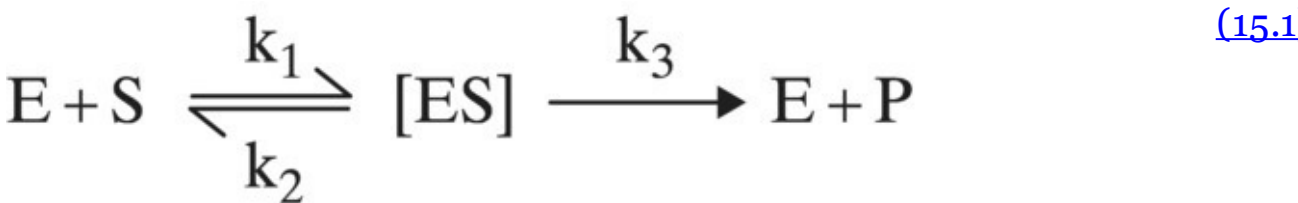
Where E denotes enzyme, and S is substrate, ES is enzyme–substrate complex and P is product.

Catalytic activity depends on the conformation of the enzymes, which is altered by the pH and temperature of the medium. Most enzymes become inactivated at extreme acidic and basic pH, and at higher temperatures due to changes in their conformation and this process is

called denaturation (Figure 15.1).
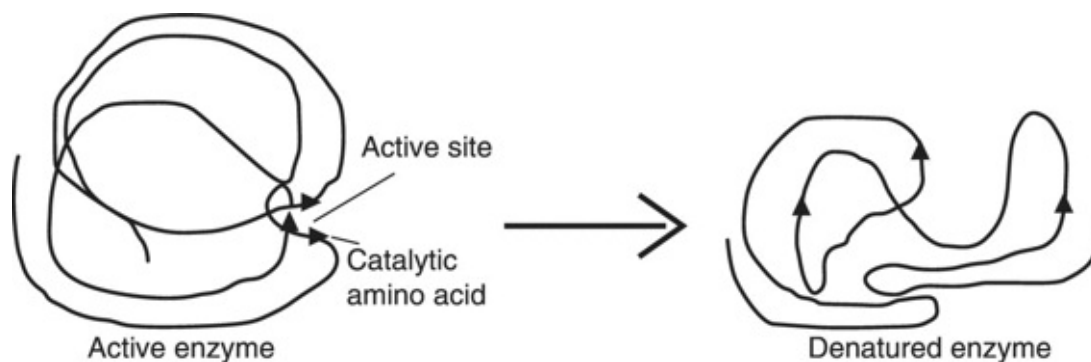
Figure 15.1 Denaturation of enzyme.

Enzyme assays and enzyme activity

The amount of enzyme present in a system (solution) can be determined (assayed) by its ability to convert substrate to product. Enzyme concentrations are more conveniently assayed by measuring the rate of appearance of product or disappearance of the substrate by a suitable analytical method. Enzyme activity is commonly expressed by the initial rate of the reaction being catalyzed. The unit of initial rate is micromole per minute (μmol/min) under defined conditions. It can also be expressed as katal. Katal is defined as the amount of enzyme required to convert one mol of substrate to its product per second. For industrial enzyme applications, enzyme suppliers often define units in terms of the technological functions of enzymes. For example, international milk clotting units (1 MCU) are used for quantifying milk-coagulating enzymes such as chymosin and rennet for their use in cheese making. The specific activity of an enzyme in a sample refers to the total number of enzyme units per milligram of protein. The molecular activity of an enzyme is termed as turnover number (K_{cat}). It can be defined as "the number of moles of substrate converted by one mole of an enzyme per minute". The activity or efficiency of an enzyme can be judged by its turnover number.

Enzyme kinetics

Enzyme kinetics is the study of the rate of reactions catalyzed by enzymes. The rate of reaction depends on (i) enzyme concentration, (ii) substrate concentration, (iii) pH and temperature of the medium, and (iv) presence of inhibitors or activators. Enzyme kinetics theory is important in order to understand the basic enzymatic reaction mechanism and to select an appropriate enzyme for its application (Fullbrook 1996).

pH optimum

Each enzyme exhibits maximum activity at a particular pH. This pH is called the optimum pH of the enzyme. For example, the optimum pH for polyphenol oxidase isolated from wheat is pH 5 (Figure 15.2a). Many enzymes work in the pH range 6–8. In general, enzymes having optimum pH in the neutral region are preferred for food applications. For a more efficient and lower cost of processing, the enzyme reaction needs to be carried out at its optimum pH.

(a)

(b)

Activity, V_0 vs Temperature (°C)

(c)

Activity, V_0 vs Substrate concentration

10 U

5 U
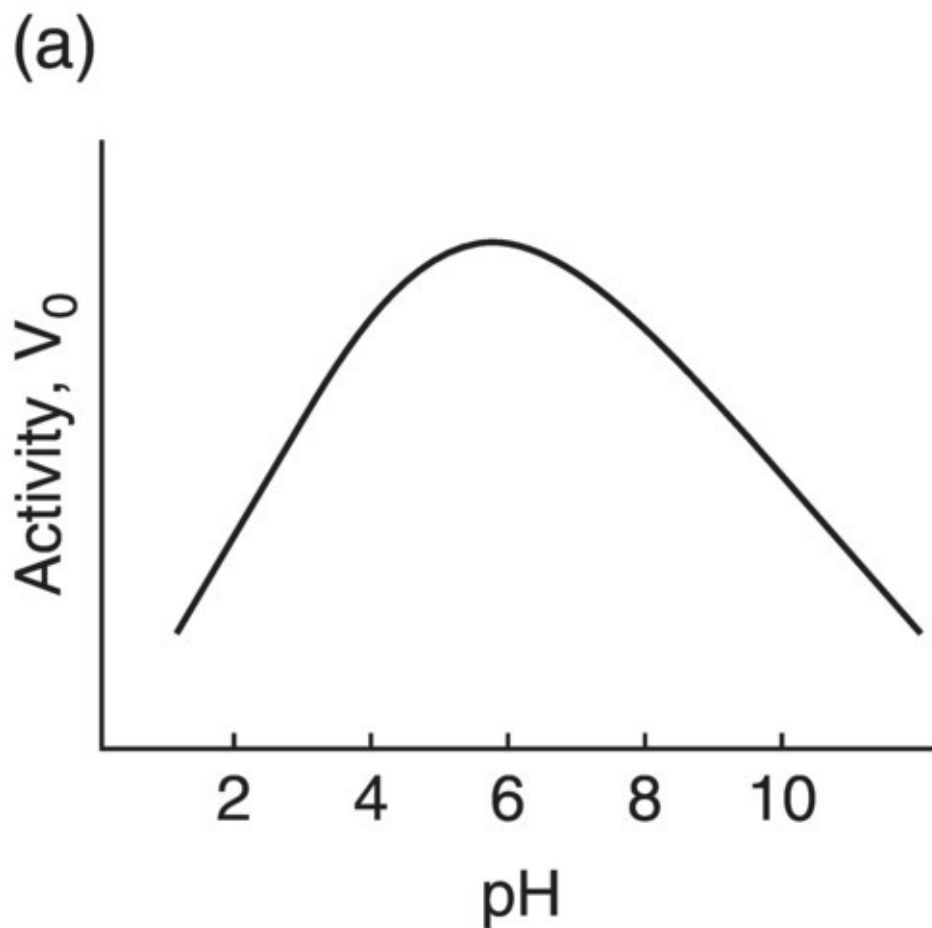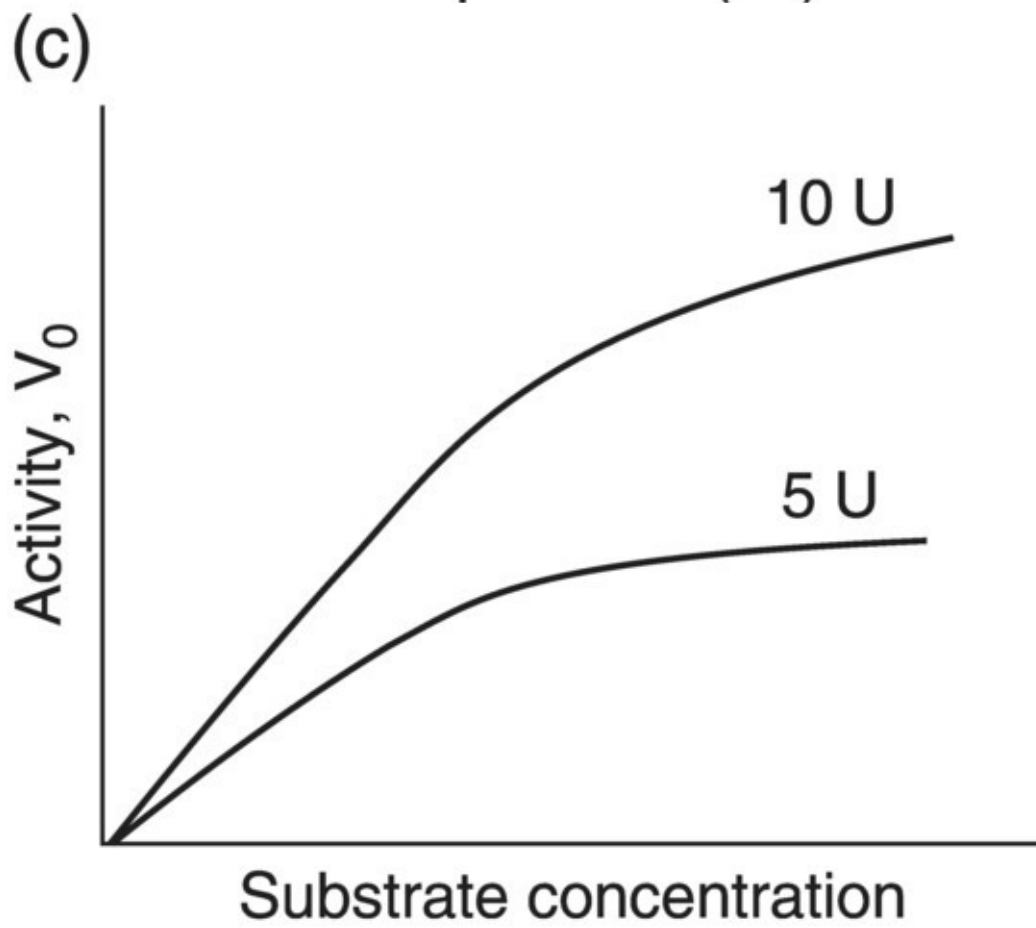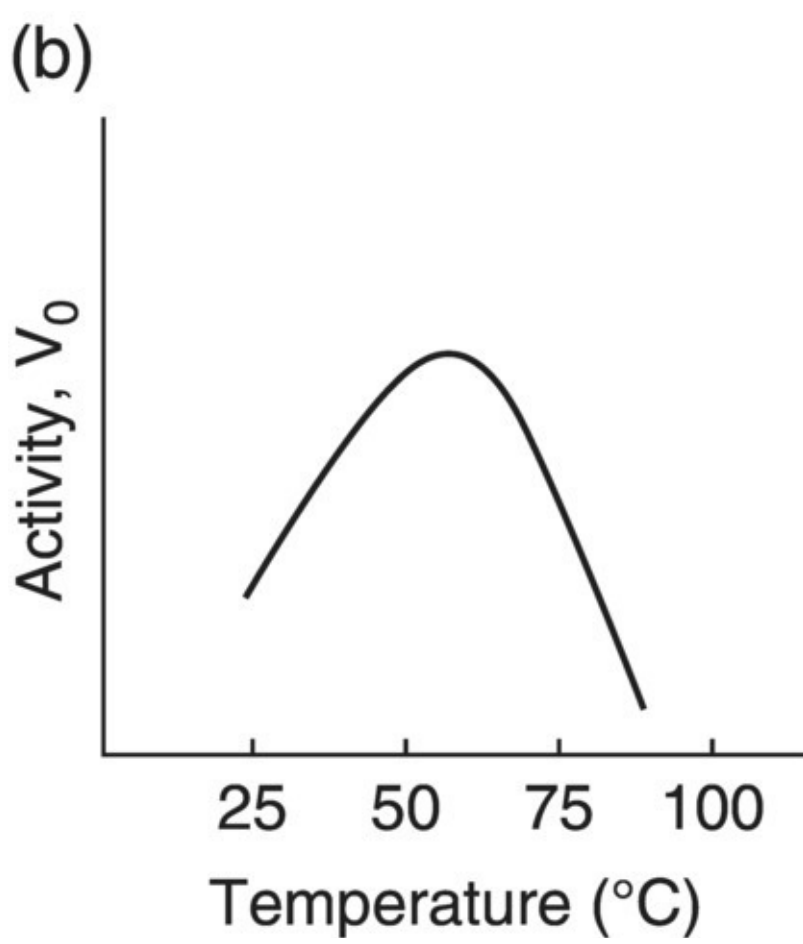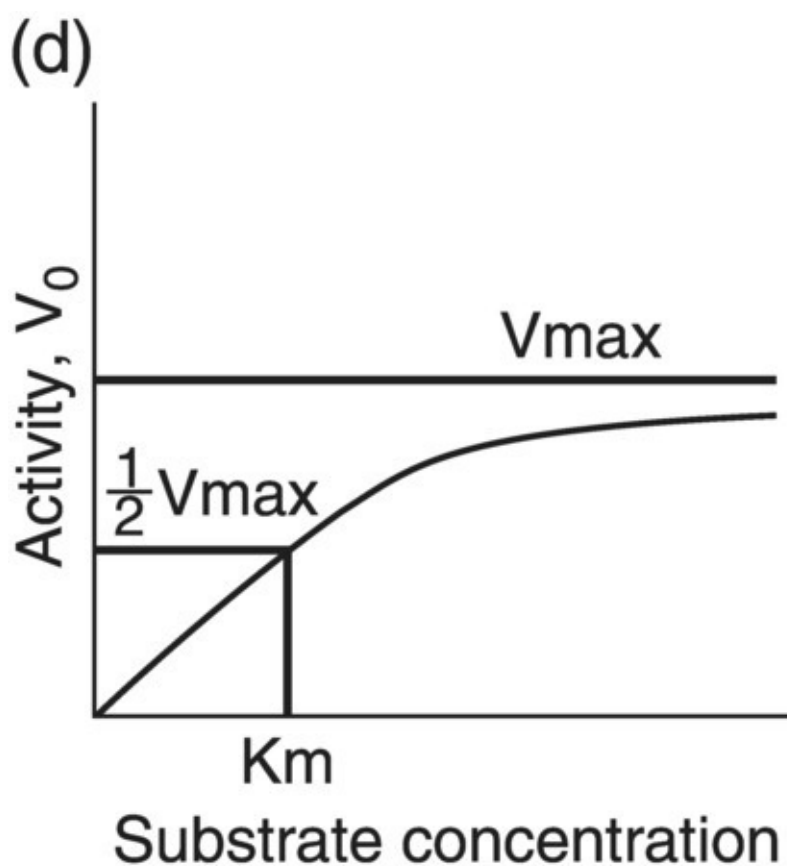
Figure 15.2 Effect of (a) pH on enzyme activity; (b) temperature on enzyme activity; (c) enzyme concentration on initial rate of velocity; (d) substrate concentration on enzyme activity.

Temperature optimum

Temperature affects the rate of the reaction in two ways: (1) a rise in temperature provides thermal energy to the substrate molecules – this will provide sufficient energy to overcome the Gibbs free energy of activation – so the rate of reaction increases; (2) at high temperatures, denaturation of the enzyme molecules takes place, thereby decreasing the rate of reaction.

As shown in Figure 15.2b, raising the temperature increases the initial velocity (V_0) or rate of reaction (first effect), and after increasing to certain temperature, the reaction rate starts decreasing (second effect). The temperature where the rate of reaction is at its maximum, is called the optimum temperature.

Effect of enzyme concentration on rate of the reaction

When the substrate concentration is higher, all the active sites on the enzyme molecules are bound by the substrate. Therefore, the rate of reaction does not depend on the substrate concentration. In this situation, the rate of reaction depends on enzyme concentration. That means if the enzyme concentration increases the rate of reaction also proportionally increases (Figure 15.2c).

Substrate concentration

At a low substrate concentration, the number of active sites occupied by substrate molecules is low. With an increase in the substrate concentration, the initial reaction velocity increases. Therefore, the reaction rate depends on the substrate concentration and the reaction velocity reaches a maximum at its optimum concentration (Figure 15.2d). At the maximum velocity, all the available enzyme molecules are converted to ES complex. Under saturation kinetics, the rate of reaction depends on the conversion of [ES] complex to product.

Enzyme inhibition

The activity of an enzyme can be decreased or completely inhibited by various compounds called enzyme inhibitors. These inhibitors bind to the enzyme molecules in such a way that the ability of the enzymes to bind to their substrates and convert to product is decreased. The enzyme inhibitors can be reversible or irreversible. Reversible inhibitors can be either competitive or non-competitive with the substrate in binding to the enzyme.

Enzyme reactions are normally carried out in dilute solutions of substrate. For substrate solutions at high concentrations, enzyme activity decreases or sometimes it may also be inactivated. Sometimes, the product formed will inhibit the enzyme-catalyzed reaction by binding to the active site. This process is called product inhibition.

Enzyme stability

Due to inherent physical instability of their conformation to various conditions such as temperature, pH, and action of inhibitors, enzymes have a finite life. As the food is a complex system containing endogenous proteolytic enzymes, and protein and non-protein inhibitors, the stability of the enzyme is important when selecting and standardizing enzymes as food additives.

Sources of food enzymes and their safety

Initially, industrially important enzymes were isolated from plants and animals. As demand for enzymes increased, microbial fermentation methods were developed for producing greater enzyme quantities. Some of the microorganisms that are widely used for the isolation of food enzymes are fungi such as *Aspergillus niger, Aspergillus oryzae*, bacteria such as *Bacillus subtilis, Streptomyces* species and yeasts such as *Kluyveromyces fragilis* and *Saccharomyces cerevisiae*. These organisms are generally recognized as safe and the enzymes are produced using good manufacturing practices (Piggott 2002). After the enzyme is isolated, its storage conditions vary depending on the nature of the enzyme. In general, the enzyme should always be stored in a cool and dry environment.

In food enzyme legislation, most enzymes are regarded as processing aids because they are added during processing for technical reasons and are often denatured by heat during processing. Permitted enzymes should be devoid of toxins, heavy metal ions, pathogenic microorganisms, and other hazards as specified by WHO/FAO Joint Experts Committee for Food Additives (JECFA). The level of the enzyme residues appearing in food are so low, they are unlikely to cause allergies. However, like all proteins, enzymes can cause allergic reactions when people have been sensitized through exposure to large quantities. For this reason, enzymes are produced as liquid, granules, capsules or as immobilized preparations to limit worker exposure. In general, enzymes are safe ingredients to work with; however, the user must understand the material and procedures for handling them (Piggott 2002).

Enzyme suppliers use genetic and protein engineering techniques to improve production, efficiency, quality, and to develop new products. As this technology can alter the fundamental properties of naturally occurring enzymes and proteins, safety assurance and surveillance methods have become more sophisticated and complicated and the engineered enzymes are mostly used in non-food applications (Liu 2010).

Endogenous enzymes in wheat flour

Wheat contains various enzymes such as α-amylase, β-amylase, glucosidase, proteases, peptidases, esterases, phytases, phosphatases, lipase, lipoxygenase, superoxide dismutase, polyphenol oxidases, peroxidase, catalase, protein disulfide isomerase, phosphorylase, ascorbic acid oxidase, and dehydrogenases (Rani and others 2001; Hemalatha and others 2007; Kruger and Reed 2008; Manu and Prasada Rao 2009). Many of these enzymes have a specific role in the preparation of wheat-based products. These enzymes improve the functional properties of the flour constituents such as proteins, carbohydrates, and lipids. As shown in Table 15.1, these enzymes are distributed in different tissues of the wheat grain, therefore – depending on the milling process – the enzyme activities in flour vary. As whole wheat flour contains bran as well as germ along with endosperm, whole wheat flour contains more of these enzymes compared to wheat flour (refined wheat flour). Reactions catalyzed by some of these enzymes will be discussed in the subsequent sections.

Table 15.1 Distribution of some of the functionally important enzymes of wheat in different tissues

Enzyme	Distribution
α-Amylase	Endosperm, bran and germ; concentrated in outer layer of endosperm and near the germ and rich in bran
β-Amylase	Endosperm, bran and germ
Protease	Endosperm, bran and germ; concentrated more in germ, followed by aleurone layer and endosperm
Lipase	Endosperm, bran and germ; rich in germ followed by bran
Phytase	Endosperm, bran and germ; rich in endosperm
Lipoxygenase	Endosperm, bran and germ; rich in germ, followed by bran
Polyphenol oxidase	Endosperm, bran and germ; concentrated more in bran and germ
Peroxidase	Endosperm, bran and germ; concentrated more in bran and germ

Compiled based on Kruger and Reed (1988); Rani and others (2001).

Role of flour constituents on the wheat flour functionality and the effect of enzymes on their functionality

Effect of proteins on functionality of wheat

The protein content in wheat flour varies from 8 to 16% depending on the variety. The quantity of protein alone cannot explain all the variations in product quality. The content and the quality of the gluten proteins present in dough mainly influence the viscoelastic property of wheat. Gluten is a mixture of water insoluble storage proteins. It constitutes about 80% of the total protein of wheat. Gluten consists of gliadins, glutenin, and insoluble glutenin (residue protein). Of these, gliadin contributes the viscous and glutenins contribute the elastic properties to dough. Gliadins are monomeric proteins, while glutenins contain several subunits linked together by disulfide bonds and secondary bonds. The changes in the content and biochemical properties of gluten proteins will greatly influence its suitability for the preparation of various products.

Baking industries do not always require hard wheat for the preparation of all types of bakery products. For bread preparation, hard wheat having a high viscoelastic property is required; for biscuit and cake preparation, soft wheat is preferred; and for chapati-making, medium hard wheat is suitable. As gluten proteins are primarily responsible for the viscoelastic property of dough, the addition of proteases breaks down the gluten proteins and produces dough with a soft and more extensible structure. On the other hand, the addition of protein cross-linking enzymes produces harder and more viscoelastic doughs due to the improved glutenin polymer structure. Normally, cross-linking enzymes are used with soft or medium hard wheat flours to yield strong dough that has an improved resistance to stretching suitable for bread. These cross-linking enzymes form covalent bonds between polypeptide chains either due to the oxidation of sulfhydryl groups, cross-linking of tyrosine residues or acyl-transfer reactions between amino acid residues. Thus, addition of any chemical compound or enzyme that modifies the structure of gluten proteins or its network will influence the dough properties and finally the end product quality.

Enzymes used for the modification of protein to yield desirable quality characteristics of dough are discussed in the subsequent sub-sections.

Proteases

Proteases can be defined as the enzymes that cleave the peptide bonds in a polypeptide or protein in an endo- or exo- manner and give small polypeptides or amino acids as products. Proteases can be classified into 4 groups based on the amino acid residues at their active site: serine proteases, cysteine or sulfhydryl proteases, aspartic proteases, and metalloproteases.

In addition to being exo- or endo-, some of the proteases cleave specific peptide bonds contributed by particular amino acid residues (specific proteases) while some of them do not (non-specific). For example, trypsin specifically cleaves peptide bonds in which lysine and arginine provide the carbonyl group (Table 15.2). Pepsin is a non-specific protease and therefore it cleaves the peptides bonds of a polypeptide chain indiscriminately. Another important characteristic feature of proteases is that their activity is pH dependent. For

example, trypsin and chymotryspin have an optimum pH around 8, pepsin has an optimum pH in acidic region between 2 and 3, while papain is active near neutral pH (around pH 6) (Table 15.3).

Table 15.2 Specific cleavage of peptide bonds of proteins by proteases

Enzyme	Specificity
Trypsin	C-terminal side of Lys and Arg
Chymotrypsin	C-terminal side of Phe, Tyr, Try, Leu
Carboxypeptidase	Hydrolyzes the first peptide bond at the C-terminal end
Aminopeptidases	Hydrolyzes the first amino acids from the N-terminal end of protein or peptide
Thermolysine	N-terminal side of hydrophobic amino acids

Table 15.3 Optimum pH of proteases

Type of protease	pH optimum

Acidic proteases
   Pepsin, chymosin
   Protease from *Aspergillus niger*
	2.0–3.0
	2.5–3.5

Thiol proteases Papain, bromelain	5–7
Metalloprotease Carboxypeptidase, aminopeptidase	around 7
Serine protease Trypsin, chymotrypsin	7.5–10

Protease is a widely used enzyme in baking industry. Proteases are added when dough is too tough or to decrease gluten strength. In bread dough, it is used to improve its softness, handling properties, machinability, and gas retention time due to its better extensibility, and to reduce mixing time. As a result of these improved dough properties, proteases yield bread with improved grain and crumb texture and with improved color and flavor (Mathewson 2000; Lindhal and Eliasson 1992). However, higher protease activities in the flour lead to degradation of gluten proteins into polypeptides resulting in loss of gluten functionality, decrease in dough consistency, and decrease in bread loaf volume.

Peroxidases

Peroxidases (EC, 1.11.1.7; donor: hydrogen-peroxide oxidoreductase) are ubiquitous in nature. In the presence of H_2O_2, it catalyzes the oxidation of a wide variety of substrates such as phenols, aromatic phenols, phenolic acids, indoles, amines, sulfonates, thiols, halides, amino acids, nicotinamide adenine dinucleotide, and reduced nicotinamide adenine dinucleotide phosphate (Richard-Forget and Gauillard 1997). As a result of oxidation, these substrates form radicals that can further react with other substrates. It uses hydrogen peroxide as an electron or hydrogen acceptor for catalyzing different oxidative reactions. The overall reaction is (Equation 15.2):

$$H_2O_2 + 2AH_2 \xrightarrow{\text{POD}} 2AH^* + 2H_2O \qquad \text{(15.2)}$$

where AH_2 is a substrate, which is a hydrogen donor.

Peroxidase modifies the amino acid side chains of proteins in many ways. In the presence of low molecular weight phenolic compounds, the o-quinones generated by the enzyme can react with amino, sulfhydryl, thioether, phenolic, indole, and imidazole groups of proteins. In some cases, these reactions will lead to protein cross-linking. In the absence of low molecular weight phenolic compounds, tyrosyl groups of proteins can serve as substrate for both the enzymes and lead to protein cross-linking (Feeney and Whitaker 1988).

Addition of peroxidase to wheat flour improves dough handling, dough tolerance, dough consistency, crumb structure, and loaf volume of bread (Van Oort 1996; Hilhorst and others 1999; Dunnewind and others 2002). The positive effect of peroxidases in baking has been attributed to cross-linking of feruloylated arabinoxylans into larger aggregates. Studies indicate that peroxidase/H_2O_2 catalyzes the oxidative gelation of arabinoxylans via the formation of diferulic acid linkages (Schooneveld-Bergmans and others 1999). Peroxidase also catalyzes the protein–protein cross-linking through disulfide as well as dityrosine bonds (Rodriguez-Mateos and others 2006; Manu and Prasada Rao 2011). In dough, such cross-linking was suggested to be responsible for the improvement of dough properties. Glutenin and gliadin proteins contain about 2% tyrosine of the total amino acid residues and some of these tyrosine residues in these proteins may form dityrosine cross-links (Figure 15.3).
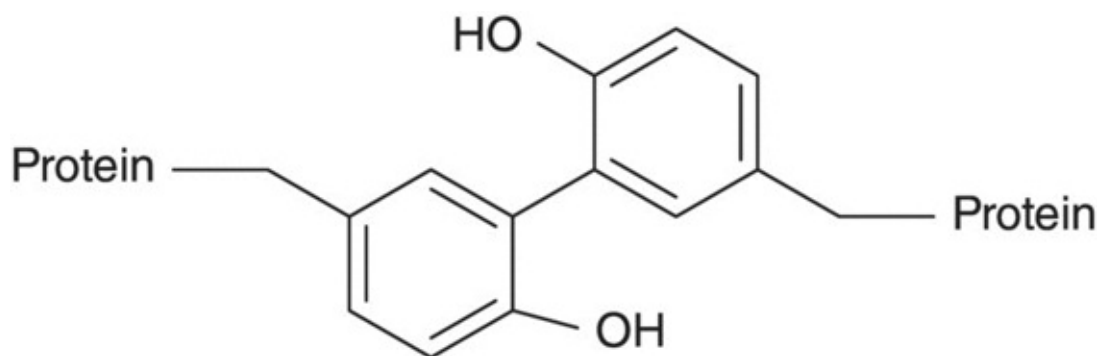
Figure 15.3 Intermolecular dityrosine cross-link in proteins.

Manu and Prasada Rao (2011) have recently reported that wheat bran peroxidase possesses both peroxidase and thioloxidase activities. This dual activity of peroxidase may be responsible for producing dityrosine and disulfide bonds in gluten proteins during dough preparation. They have proposed a mechanism for the role of peroxidase and H_2O_2 in cross-linking gluten proteins.

It was proposed that the thiol oxidase activity of peroxidase oxidizes small molecular weight thiols and produces H_2O_2. The sulfhydryl groups of glutenin proteins are oxidized non-enzymatically to disulfides by H_2O_2. Thiol oxidase activity may also use protein sulfhydryls as substrates and produce disulfide bonds. The glutenin protein network is further strengthened by the formation of dityrosine bonds, which is catalyzed by peroxidase using H_2O_2 produced by thiol oxidase activity or by other enzymatic or non-enzymatic reactions during dough formation. The mechanism proposed not only explains how H_2O_2 and peroxidase function as dough improvers but also indicates the role of endogenous peroxidase and in situ generated

H_2O_2 in dough formation.

Polyphenol oxidases

Polyphenol oxidase (PPO) is a generic term for the group of enzymes that catalyses the oxidation of phenolic compounds, tyrosine, and amines to quinones in the presence of O_2 and ultimately to brown pigments. The quinones formed are polymerized non-enzymatically in to brown pigments (Equation 15.3). Based on their substrate specificity, PPOs are designated as tyrosinase (EC 1.14.18.1), catechol oxidase (EC 1.10. 3.1), and laccase (EC 1.10.3.2). These enzymes have pH optima in the acidic range and lose their activity above 60 °C (Saby John and others 2011). Apart from browning reactions, PPOs may also be used in food processing for improving the functionality of various foods. Among the PPOs, laccase oxidizes a wide variety of substrates including o- and p-diphenol and therefore, its use in the food sector is well recognized. The general reaction for catecholoxidase and laccase is given here.
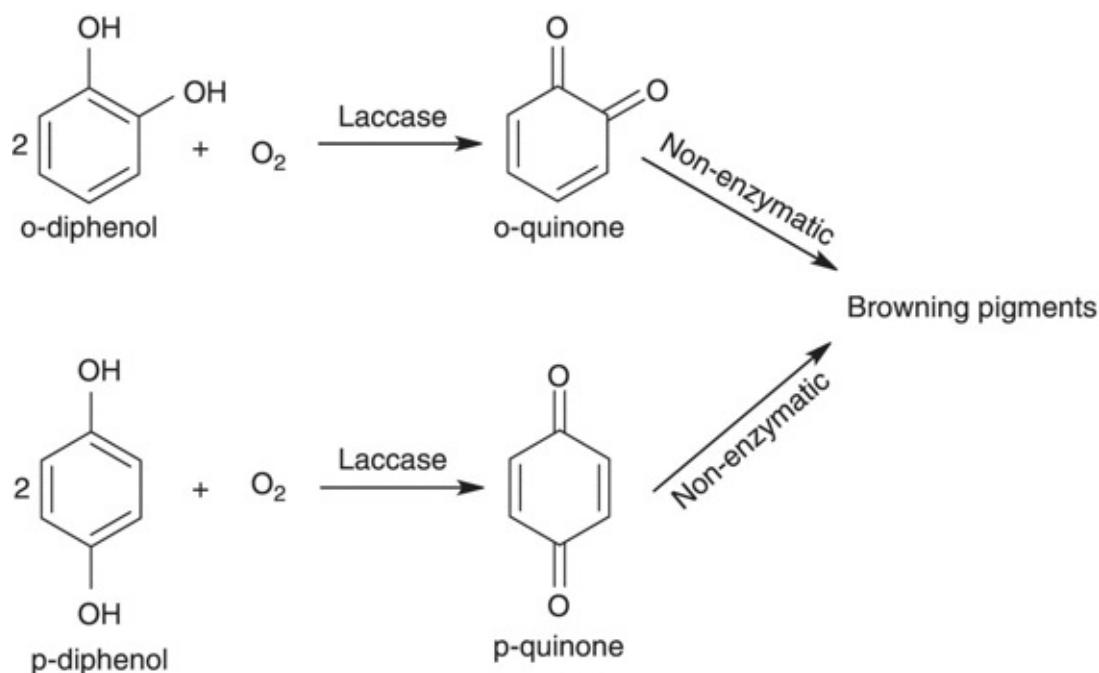
Figure 15.4 Laccase catalyzed reactions.

$$\text{Phenol} + O_2 \xrightarrow{\text{PPO}} \text{Quinone} \xrightarrow{\text{Non-enzymatic}} \text{Browning pigments} \tag{15.3}$$
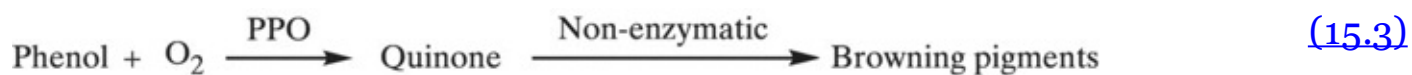
Laccase oxidizes a variety of phenolic, amine compounds and even inorganic molecules in the presence of molecular oxygen (Minussi and others 2002). One of the characteristic features of laccase compared to other PPOs is that it can oxidize o- and p-diphenol, syringaldazine, p-phenyldiamine, which are not oxidized by catechol oxidase and tyrosinase. They are common in bacteria and fungi, but their presence is very limited in higher plants (Gianfreda and others 1999). Oxidation of o- and p-diphenol reactions catalyzed by laccase is shown in Figure 15.4.

The use of laccase in baking is currently increasing because of its ability to form cross-linkages between proteins and/or carbohydrates (Minnussi and others 2002). The addition of laccase to wheat flour decreased stickiness, improved the dough machinability by strengthening the dough, and improved the texture, volume, and flavour of the bread (Si 1994).The improvement in dough characteristics were found to be greater when poor quality flours were used. One of the important reactions mediated by laccase is that it catalyses the

oxidative gelation of arabinoxylan by dimerization of ferulylated esters through ferulic acid and this property is mainly responsible for the improvement of wheat flour dough properties. These enzymes also catalyze the corss-linking of arabinoxylans with gluten proteins. Most of the enzymatic reactions catalyzed by polyphenol oxidases involve free radical mediated reactions that are metastable in the solution, that is, they exist long enough to undergo other non-enzymatic reactions. Free radicals generated in these reactions are mainly responsible for the protein–protein cross-linking, ferulic acid mediated protein–arabinoxylan interactions, and diferulated oxidation of arabinoxylans.

Glucose oxidase

Glucose oxidase (GO) irreversibly oxidizes β-D-glucose to δ-D-1,5 gluconolactone, which is immediately converted to gluconic acid (Figure 15.5). In addition to glucose, it oxidizes a number of aldose molecules such as mannose, xylose, and galactose; however, oxidation of these sugars by GO is much lower than that of glucose. Oxygen is required for this reaction and acts as an electron acceptor, which is reduced to H_2O_2 (Wong 1995). In this reaction, H_2O_2 is an important product, which acts as an oxidizing agent. H_2O_2 produced in the glucose oxidase catalyzed reaction also acts as a substrate (electron acceptor) for peroxidase, which catalyzes tyrosyl cross-link formation in proteins present in wheat flour (Tilley and others 2001). The treatment of dough with GO increased the gluten macropolymer content due to disulfide and non-disulfide cross-linking (Steffolani and others 2010).
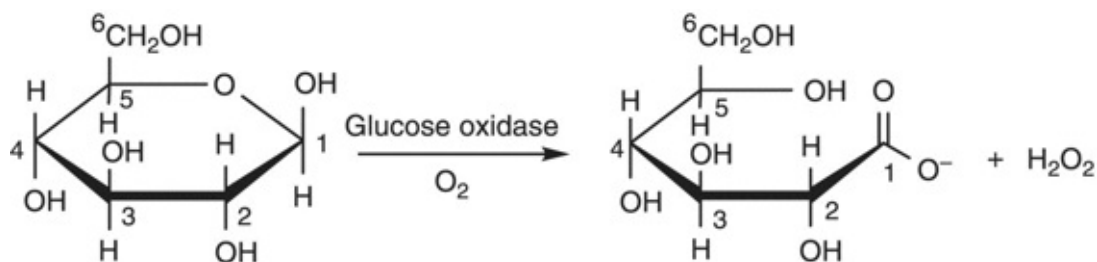
Figure 15.5 Glucose oxidase catalyzed reaction.

Use of GO for bread making has been known since 1957. It is an oxidizing enzyme used to produce stronger doughs. Incorporation of GO in flour increased the bread dough stability and resistance to extension (Indrani and others 2003). In combination with other enzymes like α-amylase and xylanase, GO can replace chemical oxidants such as potassium bromate or azodicarbonamide in some baking formulations. GO in combination with enzymes such as xylanase and α-amylase as well as ascorbic acid was reported to exhibit excellent dough strengthening effects and improved the quality parameters of French batards, Marraquetta (South American bread), and Kaiser rolls (Si and Drost-Lustenberger 2002).

Lipoxygenase

Lipoxygenase (LOX) catalyses the oxidation of polyunsaturated fatty acids containing *cis,cis*-1,4-pentadiene systems (Figure 15.6a) to produce peroxy free radicals in the presence of molecular oxygen (Figure 15.6b). The peroxy radical formed abstracts a hydrogen atom from another fatty acid molecule and forms hydroperoxides (Figure 15.6c).This enzyme-catalyzed reaction exhibits substrate specificity, positional specificity, and stereospecificity. Linoleic acid, linolenic acid, and arachidonic acid and their esters are substrates for this enzyme.
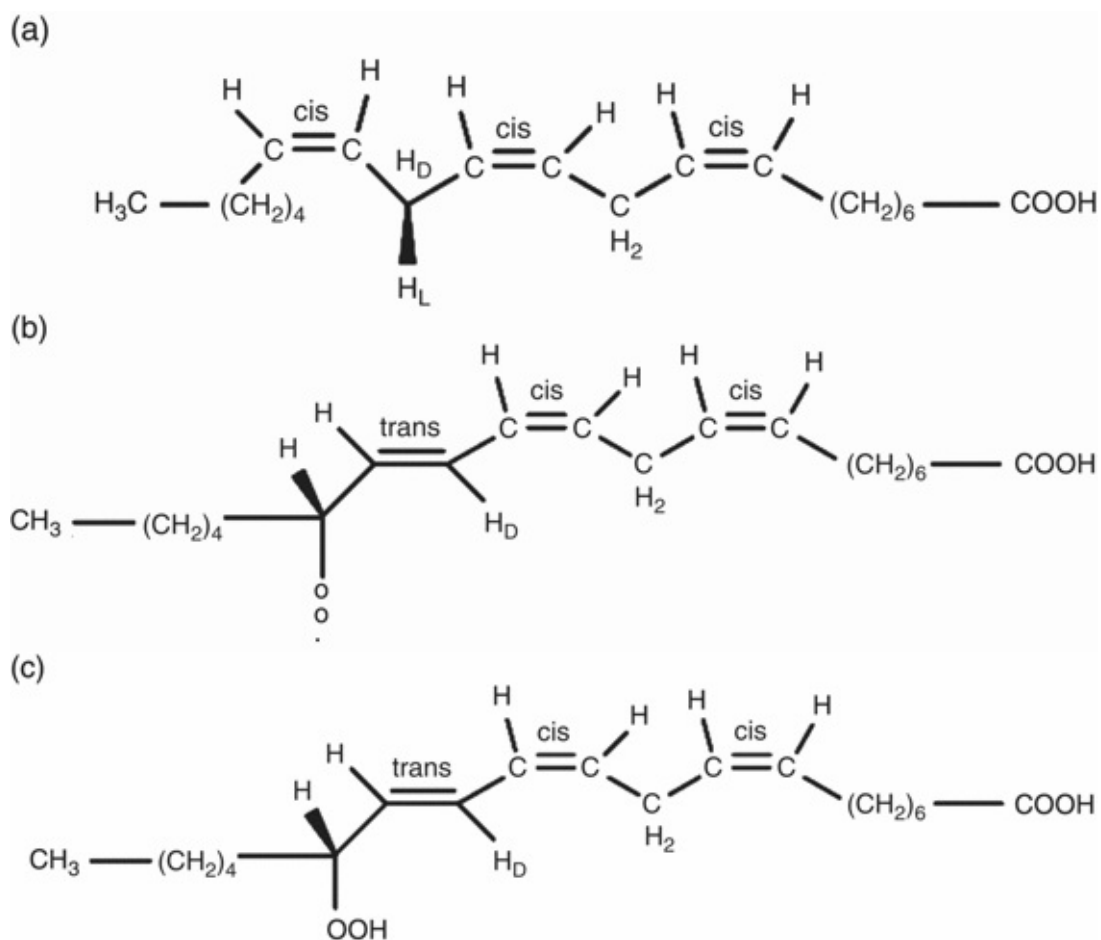
Figure 15.6 Reaction catalyzed by lipoxygenases: (a) unsaturated fatty acid; (b) peroxy radical; (c) hydroperoxide.

LOX from soy flour has been used as a bleaching agent as well as a dough conditioner to improve the viscoelastic property of dough (Junqueira and others 2007). The hydroperoxides formed from unsaturated fatty acids react with yellow carotenoids present in wheat flour and reduce the yellow color. This bleaching reaction is desirable in bread preparation to obtain white crumb. However, it is undesirable for pasta products. Soy bean LOX showed a positive effect on bread loaf volume due to the improvement in gluten viscoelasticity. This improvement may be due to the oxidation of sulfhydryl groups of gluten protein into disulfide bonds by hydroperoxides (Avram and others 2003).

Transglutaminase

Transglutaminase catalyzes the formation of isopeptide bonds between the side chains of the glutamine and lysine residues of proteins. In this reaction, γ-carboxyamide groups of glutamine residue in proteins are the acyl donors and ε-amino group of lysine residue in protein acts as an acyl acceptor (Figure 15.7). Transglutaminase (TG) has been shown to catalyze cross-linking of a number of proteins, for example milk proteins, soy protein, and collagen (Jaros and others 2006). This enzyme is used in certain foods to obtain a better texture and it has been used in bakery products to improve their quality. The important commercial source for TG is guinea pig liver (Zhu and others 1995).
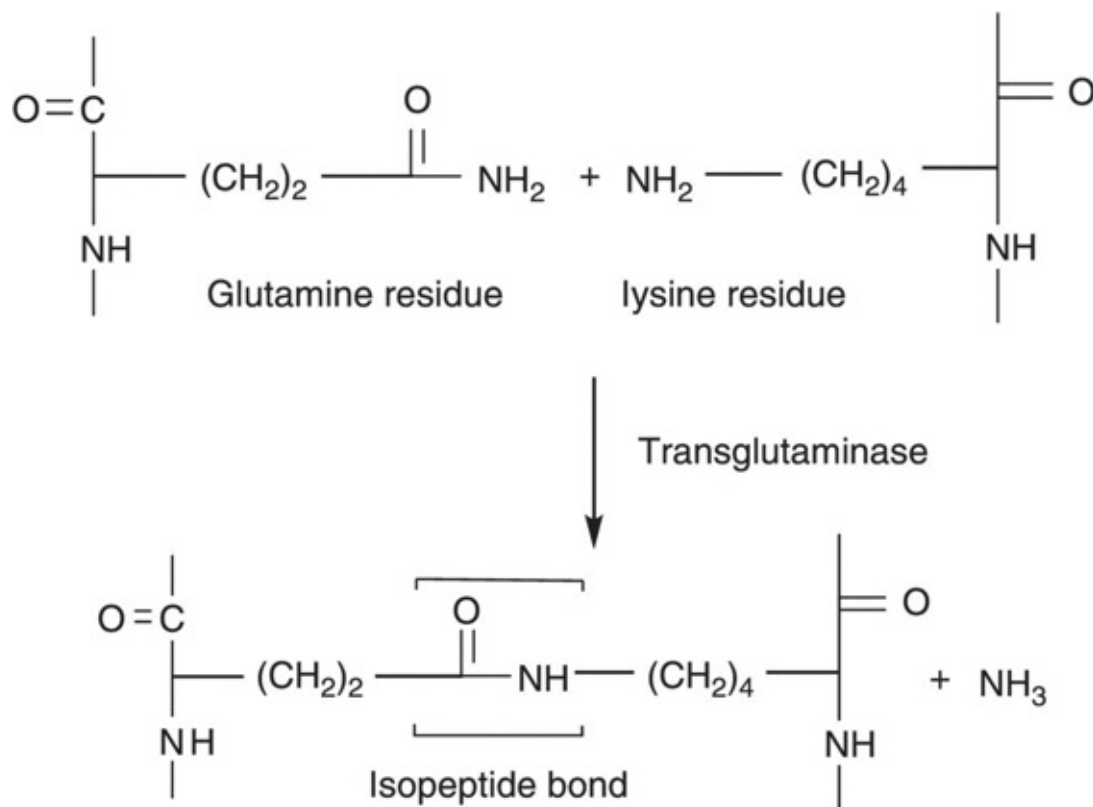
Figure 15.7 Transglutaminase catalyzed reaction.

TG is added to weak flours to obtain gluten with more elastic properties with increased dough resistance and reduced extensibility which are characteristic of strong dough (Li and others 2011). Unlike oxidative enzymes, TG does not oxidize thiol groups to disulfide bonds and, the cross-linking reactions are independent of redox system of the dough. However, the dough strengthening properties are comparable to $KBrO_3$ or enzymes that oxidize thiol groups (Gottmann and Sproessler 1995). Among the gluten proteins, HMW glutenin subunits can form a greater number of ε-N-(γ-glutamyl)-lysine cross-links compared to gliadins as glutenins contain more amount of Lys (2.1 mol % of the amino acid content) compared to gliadins (0.8 mol %) (Belitz and others 2004). TG has been used in the preparation of gluten-free foods because of its ability to form isopeptide bonds between proteins (Moore and others 2006).

Effect of starch on functionality of wheat

Starch constitutes about 65–70% of wheat flour (D'Appolonia and Rayas-Duarte 1994). During milling of the grain, a significant amount of starch is converted into damaged starch. The damaged starch content can be as low as 8–16% depending on the wheat variety and milling conditions (Hemalatha and others 2007). Amylases act on the damaged starch present in the flour and release sugars. These sugars are utilized by yeast during fermentation of the dough to release CO_2 and also to provide a better crust color and an improved flavour, due to the Maillard reaction.

α-Amylases

α-Amylase is an endoglucosidase that cleaves 1,4 glucosidic bonds of starch at an internal position to yield dextrins and oligosaccharides. Wheat contains endogenous amylase activity and the activity varies from variety to variety. The level of amylase activity is lower in normal

wheat compared to germinated wheat (Van Dam and Hille 1992). As normal wheats are used for the preparation of bread, it is a common practice to supplement the α-amylase in bread flours with either fungal amylases or malt flour. It has been reported that an increase in amylase activity, increased the bread loaf volume and crumb structure (Goesaert and others 2009). However, at higher dosage, the dough becomes too sticky to handle and this will affect the bread quality. Therefore, supplementation of amylases should not exceed its optimum levels. Si and Drost-Lustenberger (2002) reported that the optimum dosage for two different flours was found to be around 15 FAU/kg flour (FAU = fungal α-amylase units).

One of the important functions of α-amylase in wheat flour in bread making is to produce fermentable sugars (glucose) from starch to produce CO_2. Wheat flour contains 0.5% of fermentable sugars, which is not sufficient for optimal yeast growth and carbon dioxide production. The presence of α-amylase in flour produces fermentable sugars by the breakdown of starch and also reduces bread staling. During bread aging, its crumb becomes firm, dry, and loses its fresh odor and this phenomenon is referred as staling (Hebeda and others 1990). Staling is mainly attributed to the retrogradation of starch. Addition of α-amylases prevents starch retrogradation by hydrolyzing starch (Hug-Iten and others 2003). Antistaling effect of α-amylase is reported to be due to hydrolysis of glycosidic linkages within the amorphous regions of gelatinized starch (Gil and others 1999).

Effect of arabinoxylans on functionality of wheat

Arabinoxylans (pentosans) are the major non-starch cell wall polysaccharides of wheat. They constitute 5–8% of the wheat grain (Pritchard 2011). Although flour contains a low amount of arabinoxylans, they are important components of dough because of their high water holding capacity, which is as much as 10 times their weight in water. Arabinoxylans affect the rheological properties of dough, and textural and other quality parameters of the baked end-product (Courtin and Delcour 2002). Arabinoxylans contain mainly arabinose and xylose: a linear (1 → 4)-ß-xylan backbone to which arabinose residues are attached at the C(O)2 and/or C(O)3 position. Ferulic acid can be linked to C(O)5 of the arabinose through an ester linkage (Courtin and Delcour 2002).

Xylanases

Water-soluble arabinoxylans content was positively correlated to bread quality, while insoluble arabinoxylan content resulted in decreased bread loaf volume (Krishnarau and Hoseney1994). Treatment of bread dough with xylanases increases the bread quality, due to increase in water soluble arabinoxylans. Although an increase in xylanase incorporation in dough yields bread with a higher volume, it gives sticky dough, which is difficult to handle. However, a combination of xylanase with fungal α-amylase was reported to yield bread with increased volume and increased overall quality scores with better dough handling properties (Si and Drost-Lustenberger 2002). Also, addition of xylanase to flour retards bread staling due to the interaction between arabinoxylan and starch (Rouau and others1994; Poutanen 1997).

Effect of lipids on functionality of wheat

Lipids are structurally diverse group of compounds, but all lipids contain fatty acids and are

insoluble in water but soluble in organic solvents. Acylglycerols (triglycerols) are the most abundant group of naturally occurring lipids. Compared to starch, arabinoxylans, and protein, the lipid content in wheat is low. It constitutes about 1–2.5% of the wheat flour. However, lipids are reported to contribute significantly to the bread quality. Lipids form complexes with amylose during baking that result in a soft bread crumb (Pareyt and others 2011). Wheat flour contains both polar and non-polar lipids, but polar lipids represents 70–75% total lipids (Pareyt and others 2011).These lipids can be further subclassified into free and bound lipids. Free and bound lipid contents were reported to influence the end-use quality of flour. The presence of high levels of free polar lipids yields bread with a superior quality (Panozzo and others 1994).

Lipase

Lipase is a lipid hydrolyzing enzyme. It hydrolyzes various glycerides such as triacylglycerols, diacylglycerols, and monoacylglycerols. It is reported to be a strong dough conditioning agent. Lipase improves the dough handling properties similarly to emulsifiers such as DATEM or sodium steroyl-2-lactate (SSL) possibly by modifying the gluten and starch structures (Colakoglu and Ozkaya 2012). Gluten isolated from lipase-treated dough was reported to be more elastic than the control. However, how lipase produces these effects is not fully understood. The addition of lipase yielded bread with increased loaf volume, a silky and uniform crumb structure, and with a white appearance. The addition of lipase with xylanase and α-amylase improved the bread dough stability and crumb structure due to their synergistic effect. The monoglycerides produced by lipase are reported to exhibit an antistaling effect by forming complexes with starch (Si and Drost-Lustenberger 2002).

Use of enzymes in few non-bread, wheat based products

All the enzymes described earlier are known to improve bread quality. The knowledge gained on the use of enzymes in bread making are being applied to improve the quality of non-bread wheat-based products. This area is growing rapidly and is covered in the following sections.

Chapati

Chapati is a single-layered, unleavened flat bread that is the staple diet of most of the population in the Indian subcontinent, and it is also widely consumed in the United Kingdom and in other countries by the Asian ethnic community. It is prepared from whole wheat flour obtained by grinding wheat in a plate mill (Chakki) or from the resultant atta, a by-product of the roller flour-milling industry. Preparation of chapati involves kneading the flour with 60–75% water to obtain smooth, cohesive, and non-sticky dough, and the dough is rested for minimum of 15–30 min before it is sheeted to 2–3 mm thickness. The dough thus sheeted is cut into a circular shape with a diameter of 10–15 cm and baked on a hot plate at 220 °C for about 1–2 min followed by puffing on a live coal fire or on flame for few seconds. Chapati contains mostly crust but little or no crumb. Desirable quality parameters for chapati are that it should have a soft, puffy, and pliable texture with chewy characteristics (Haridas Rao 1993; Hemalatha and others 2007).

Earlier studies indicated that 9.5–10.5% protein was suitable for making chapatis with desirable quality (Austin and Ram 1971); however, subsequent studies indicated that even wheat with a higher protein content (>12%) was also suitable for good chapati preparation (Srivastava and others 2003). Ram and Nigam (1981) reported that chapati quality was influenced by the ratio between the sum of gliadins and glutenin and the residue protein (insoluble glutenin). However, no correlation was observed between the HMW glutenin subunit composition and overall chapati quality (Srivastava and others 2003; Hemalatha and others 2007).

Peroxidase and polyphenol oxidases are endogenously present in wheat flour and higher activities of these enzymes in flour may result in higher dough strengths, which yield chapatis with a leathery texture, and also cause browning of the dough, ultimately producing darker chapatis (Hemalatha and others 2007).

The addition of amylases and xylanases to chapati dough improved the softness and pliability of chapatis (Shaik and others 2008; Hemalatha and others 2010). The desirable textural improvements in chapati may be because amylases reduce the connectivity between crystallites in the continuous starch phase by hydrolyzing starch, thus decreasing the size of the crystals (Boyle and Hebeda 1990; Hug-Iten and others 2003). On the other hand, xylanases cleave the arabinoxylan backbone, which results in alterations in the functional properties of arabinoxylan. Xylanases also remove arabinoxylan that interferes in formation of the gluten network by transforming the hydrated arabinoxylan that was bound to gluten in to smaller oligomers (Primo-Martin and others 2005). This could be one of the reasons why xylanase improves the softness of the chapati.

Amylases and xylanases also improve the nutraceutical content of products. Recently, Hemalatha and others (2012) have reported the changes in nutritional, nutraceutical, and

antioxidant properties of chapatis prepared from dough treated with amylases and xylanase. The addition of amylases and xylanases to chapati dough improves the antioxidant properties of chapati by increasing the soluble polyphenol content while the addition of α-amylases increases the soluble dietary fiber content in chapatis.

Chapatis are normally consumed hot, immediately after preparation. The texture of chapati becomes progressively harder with storage. They become stale faster than bread, possibly due to their larger surface area compared to bread. Stale chapati is difficult to chew, pliability decreases and the typical wheatish aroma decreases. Shaik and others (2008) studied the antistaling properties of different additives, for example SSL, glycerol monostearate, propylene glycerol, sorbitol, α-amylase, xylanase, maltodextrin, and guar gum. They reported that chapati staling was inhibited by all the above additives to different extents, but maltodextrin was found to be more effective in preventing staling. However, among the combinations used, SSL (0.375%) + α-amylase (100 ppm) was found to give the best textural value due to the synergistic effect.

Parotta

Two different types of parottas, namely south Indian parotta and north Indian parotta, are prepared in India. The type of wheat flour used for these two types of parotta is different. For South Indian parotta preparation, wheat flour (refined flour) is used, while for North Indian parotta, whole wheat flour is used.

South Indian parotta is an unleavened, multilayered, and circular-shaped flat bread, and effect of enyzmes on South Indian parotta quality was reported. Parotta dough is prepared by mixing wheat flour, salt, water, and oil. Sugar and egg are optional ingredients. The prepared dough is rested for 30 min and sheeted into a thin film by applying vegetable refined oil. The film is then folded into multiple layers and then coiled. The coiled dough is sheeted again in to circular shaped disc of about 15 cm diameter and 0.5 cm thickness and baked on a hot plate maintained at about 230 °C for 2 min while turning for 15 s. The baked product is creamish white with light brown spots on its surface and possesses several layers. It is a soft-textured product with chewy characteristics (Prabhasankar and others 2004).

Indrani and Venkateswara Rao (2000) reported that flour protein content was significantly correlated to the overall quality score of parotta. The addition of potassium metabisulfite (100 ppm) or l-cysteine (50 ppm) improved the quality of parotta, while above these concentrations, that is 200 ppm of potassium metabisulfite and 100 ppm of cysteine, they adversely affected the parotta quality (Indrani and Venkateswara Rao 2006).

The addition of xylanase and proteinases has increased the overall quality of parotta while the addition of GO and fungal α-amylase decreased overall quality (Prabhasankar and others 2004). They speculated that breakage of the protein fibril by proteinases might increase the quality of parottas.

Pasta products

Pasta products such as spaghetti, macaroni, and vermicelli are traditional cereal-based products. They are popular all over the world because of their convenience, nutritional quality, and palatability (Cubadda 1994). Durum wheat is suitable for making pasta products,

mainly due to its the high pigment content and protein content. A high level of yellow pigment in durum wheat does not necessarily yield a more yellow color. The color of the product is also influenced by the high activities of LOX, polyphenol oxidase and peroxidase.

Pasta made from durum wheat cultivars of superior quality yields a bright yellow color and the color is retained after cooking. Pasta made from durum wheat also gives better cooking quality, firmness, resistance to surface disintegration, and desirable flavor and stickiness. LOX causes oxidative degradation of yellow pigments and pigment loss is significantly correlated to the presence of LOX activity (Fares and others 2001). Pasta products made from wheat cultivars having high PPO and POD activities have been implicated in the development of an undesirable brownish color during processing (Fraignier and others 2000).The carotenoid pigment degradation by LOX is not desirable even from the health point of view as carotenoids protect the cell membrane from injuries by quenching reactive oxygen species (Pan and Ho 2008), with a consequent possible role in the treatment of human diseases (Olson and Kobayashi 1992). In addition to oxidative enzymes, TG influences the quality parameters of spaghetti. Aalami and Leelavathi (2008) demonstrated that addition of microbial TG improved the quality parameters of spaghetti prepared from low protein-poor variety of wheat. Protein cross-linking catalyzed by TG resulted in changes in the pasting properties of semolina, dough properties, the cooking quality properties of dry as well as cooked spaghetti, and the microstructure of cooked spaghetti. Addition of microbial lipase also improved the breaking strength of dry spaghetti, and the firmness and stickiness of cooked spaghetti samples.

Biscuits, cakes, and muffins

Biscuits and cookies

For biscuit or cookie making, soft wheats are normally used. The soft wheat produces a larger cookie spread as the dough becomes less viscous during baking. Chemical or enzyme ingredients are used for different types of biscuits, mostly in semisweet and salt biscuits. The main ingredients in semisweet biscuit dough are wheat flour, fat, sugar, and water. To improve the rheological properties of dough, gluten modifying agents are used. The most commonly used chemical is sodium metabisulfite, which cleaves the disulfide bonds into sulfhydryl groups of gluten and other proteins present in the flour, resulting in increased dough extensibility and a decrease in elasticity (Stauffer 1994). The addition of proteases to flour improves the dough handling properties and functionality of dough. In the biscuit industry, proteases – which have optimum activity in neutral range (pH 6–8) – are used. Gains and Finney (1989) reported that the spread of cookies was affected by the type of flour and the nature of the protease. Therefore, one must consider the flour quality, pH optimum, temperature stability, and half-life of the enzyme at that temperature and pH. Normally, the baking industry uses bacterial proteases as they possess optimum activity at neutral pH. The addition of α-amylase or protease to biscuit dough improves biscuit quality parameters such as an increase in spread as well as the thickness of the biscuit. It was suggested that the increase in biscuit quality was due to a reduction in elasticity, which was the result of reduced gluten development. Gaines and Finney (1989) reported that papain-treated hard spring wheat flours and hard red winter flours produced higher cookie spreads compared to untreated flours and were comparable to cookie spreads made from soft red winter wheat flours. For salted biscuits, amylases are used to produce fermentable sugars and proteases are

used to modify the gluten characteristics.

Cakes

Wheat flour, sugar, and eggs are the raw materials for cakes preparation. Egg is an important ingredient and when the amount of egg is reduced, the cake quality deteriorates. This deterioration can be overcome by the addition phospholipases to the cake batter. Cake batter may be considered as an oil-in-water emulsion. Egg contains lecithin, which contains phospholipids such as phosphatidylcholine and phosphatidylethanloamine, and these lipids stabilize the emulsion by acting as emulsifiers. The treatment of batter with phospholipases further improves the emulsifying properties of these lipids by hydrolyzing them into lyso form. Presence of phospholipases in cake batter was reported to improve the cake crumb structure (Haesendonck and Kornbrust 2008). Amylases together with SSL, GMS or calcium steroyl-2-lactylate are added to control staling of cakes (Lui 2005). The addition of proteases to batter was also reported to improve the shelf-life of cakes by retarding staling (Arnaut and others 2007)

Muffins

Muffins are categorized under fat-rich bakery products similar to cakes, but normally they are not as sweet as cakes. They may be filled with sweet fillings, such as chocolate, toffee, lemons or blueberries. In muffins, about 10% fat is used as an additive to obtain muffins with a tender, low moisture, and yellow crumb. Muffins can also be made with fat substitutes. However, when fat substitutes were used, muffins were found to be the least tender (Pong and others1991). The addition of enzymes such as protease, and fungal and bacterial amylases yield muffins with texture and other sensory properties comparable to fat-containing muffins. The addition of enzymes also reduced staling, and bacterial amylase decreased the rate of staling (Hebeda and others 1990; Confort and Canterella 1998).

Use of enzymes in gluten-free products

Most bakery products are prepared using either wheat flour (refined flour) or whole wheat flour (atta) and therefore they contain gluten. One in 2000 people in the United States have celiac disease (CD). These patients are allergic to the consumption of gluten-containing foods. Therefore, CD patients have to follow a very strict diet and avoid products which contain wheat. Wheat prolamins (gliadins) or related proteins such as hordeins (barley) or secalin (rye) are reported to be responsible for CD and avoidance of these cereals leads to a recovery from the disease.

As gluten is an important functional protein that contributes to the quality of various wheat-based products, it is difficult to prepare bread, chapati, pizza or pasta products without wheat. However, some products such as biscuits, cakes or high-fat bakery products in which gluten network formation may not be essential, can be made without gluten by substituting it with gums such as guar, or xanthan gum, and so on. Bread can be made using some plant proteins and the addition of cross-linking enzymes. The addition of various enzymes such as amylases, proteases, hemicellulases, lipases, TG and oxidases are reported to improve the quality of baked goods. Using TG, gluten-free breads were made by substituting wheat flour with soy flour, egg powder or skim milk powder (Moore and others 2006). As mentioned in an earlier section, TG forms cross-links between the ε-amino groups of lysine residues and the carboxyl group of the γ-glutamyl residue of proteins and forms intramolecular as well as intermolecular peptide bonds. The protein network formed by these covalent linkages traps the CO_2 released during yeast fermentation and retains it during baking. Thus, the protein network formed by other plant proteins in presence of TG functions in a similar way to a gluten network. The addition of GO was reported to improve the breadmaking quality of rice flour (Gujral and Rosell 2004).

Conclusions

Many exciting changes are happening in the food industry as a result of improvements and innovations in the use of enzymes, either those endogenous to the material or those added exogenously as a processing aid. Enzymes with the most technological importance in the baking industry are amylases, proteases, oxidases, transglutaminase, xylanase, and lipase. In wheat dough preparation, exogenously added enzymes can improve dough handling and its machinability, product quality, minimize the varietal differences in wheat flour, and can replace chemical ingredients. While use of enzymes in bread-making is well established, their use in non-bread wheat-based products is currently being explored and this has a great potential for commercialization.

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16
Other Functional Additives

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Introduction

Functional additives have been used in the bakery sector for almost a century. Today the selection of emulsifiers, enzymes, oxidizing and reducing agents has been extended because of the evolution of bakery equipment and processing and because of a better knowledge of the complex mechanisms of flour and dough. The various additives are developed to compensate for variations in the processing characteristics of flours. They improve the machinability of doughs, simplify the process, improve the quality of baked goods and extend their shelf-life.

Oxidizing and reducing agents

At the beginning of the 20th century a number of oxidizing agents (for example, potassium bromate, ascorbic acid, azodicarbonamide, and ammonium persulfate) added to flour, in small quantities, seemed to have a major effect on the baking performance. These products improved the fermentation, the elasticity, and stability of the dough. Dough became stronger, oven rise was larger, and crumb grain became fine.

Oxidizing agents or maturing agents are products that have an effect on the gluten proteins of flour. They change the gluten characteristics from weak into stronger gluten. They promote the formation of disulfide bonds because of the oxidation of thiol groups. By creating additional disulfide bonds in the gluten, the oxidizing agents strengthen the gluten network and shorten mixing time. Addition of oxidizing agents accelerates the natural aging or oxidizing of the flour. In earlier days freshly harvested wheat had to rest for a while to allow for the maturing process. Freshly milled flour (green flour) also needed a storage period of a few weeks.

Oxidizing agents are producing oxygen by reaction. Oxygen reacts with the thiol groups oxidizing them into disulfide bonds. The reason for using oxidizing agents is the advantage of immediate consumption of fresh wheat and flour.

Oxidizing agents also have a complementary effect on the color of flour: they bleach flour by oxidizing the carotene and xanthophyll pigments.

The use of oxidizing agents depends on legislation, flour quality and production process. In European countries only ascorbic acid is permitted.

Potassium bromate

Potassium bromate ($KBrO_3$) is a slow-acting oxidant that attains its full development in the oven (oven spring). It needs a higher temperature to react and is important for the production of pan loaves. Potassium bromate is a very powerful agent, and it has to be dosed precisely because an overdose creates firm, tight doughs and breads will have a small volume with an uneven grain and large holes. Under-oxidized doughs will be weak, soft, sticky, and extensible, making them difficult to machine and process (Stear 1990). Potassium bromate (pure) is added in a concentration of 1–8 g/100 kg flour and has a particularly improving effect on the gas retention of the dough (improved gas-cell structure and loaf volume). For decades, potassium bromate has been used in flour as a protein strengthener and bleaching agent. In the fifties researchers found that carcinogenic compounds were built up between flour components and bromate. More recently, some reports have associated bromate with possible health risks (Panozzo and others 1994). Since then, the use of bromate has been reduced.

Potassium iodate

Potassium iodate is a fast-acting oxidant that increases dough consistency almost immediately after mixing and development and commencement of the floor time. It has a large effect on the gas retention in that stage and is a useful oxidant for hearth loaves.

Potassium iodate is often used in combination with potassium bromate: one part iodate with three parts bromate.

Calcium iodate ($Ca(IO_3)_2$) has a minor solubility but releases more oxygen and is active for a longer time.

Azodicarbonamide

Azodicarbonamide is a maturing agent used in a premix. It is fast acting and provides immediate oxidation when water is added. It has no effect in the dry form. Azodicarbonamide is longer acting then potassium iodate. It needs a shorter mixing time in a continuous process. Often, one part of azodicarbonamide is used in combination with two parts of potassium bromate, which results in improved dough consistency and increased mixing tolerance. Azodicarbonamide is added between 0.5–2 g/100 kg flour and increases the gas retention.

Ascorbic acid

Ascorbic acid is one of the most used oxidizing agents in flour. Ascorbic acid is added to flour as an oxidant and is as fast acting as potassium iodate. It is even more tolerant to mixing and overoxidizing and causes no mixing problems. There are two theories about enzymatic oxidation and ascorbic acid in flour. The best-known theory is ascorbic acid acts as a reductant. In flour, ascorbic acid (AsA) is converted to dehydroascorbic acid (DHAsA) by an enzyme, ascorbic acid oxidase (AsAOX), that is native to flour. Oxygen is captured in the dough during mixing and is necessary for the oxidation of AsA to DHAsA. During this oxidation there is also a reduction: the electrons coming from ascorbic acid are captured by oxygen, which will be reduced to water (Figure 16.1). Dehydroascorbic acid will act as a real oxidant. Two end-standing thiols of the gluten proteins will be oxidized, forming a disulfide bond. Since oxygen is needed, ascorbic acid is only active for a few minutes after mixing.
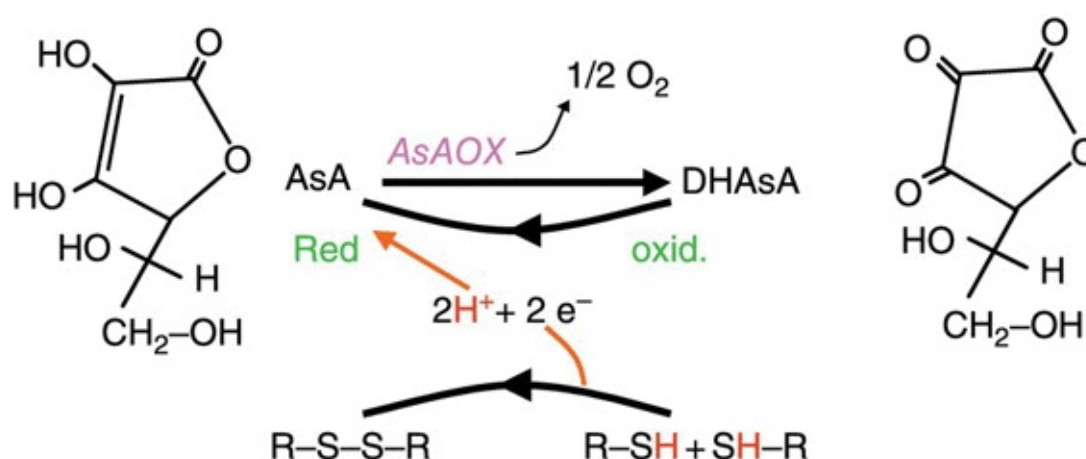
Figure 16.1 The oxidizing effect of DHAsA.

A second theory is that the action of ascorbic acid as an improver results from a reaction sequence that leads to a rapid removal of the endogenous glutathione (GSH). Otherwise, the latter chemical would cause dough weakening by sulfhydryl–disulfide interchange reactions with gluten proteins.

In the presence of oxygen, ascorbic acid is oxidized to DHAsA. This reaction is catalyzed by

ascorbic acid oxidase (AsAOX). Dehydroascorbic acid will act as an electron acceptor, and the enzyme glutathione dehydrogenase (GSH-DH) will catalyze the oxidation of glutathione, forming disulfide bonds (Figure 16.2). Because of the formation of a disulfide bond, the glutathione is no longer able to weaken the dough. Two cysteine residues can reduce the disulfide bond between oxidized GSH (GSSG) molecules with the formation of CSSC (cysteine) and free GSH. The latter compound will give the dough more extensibility.
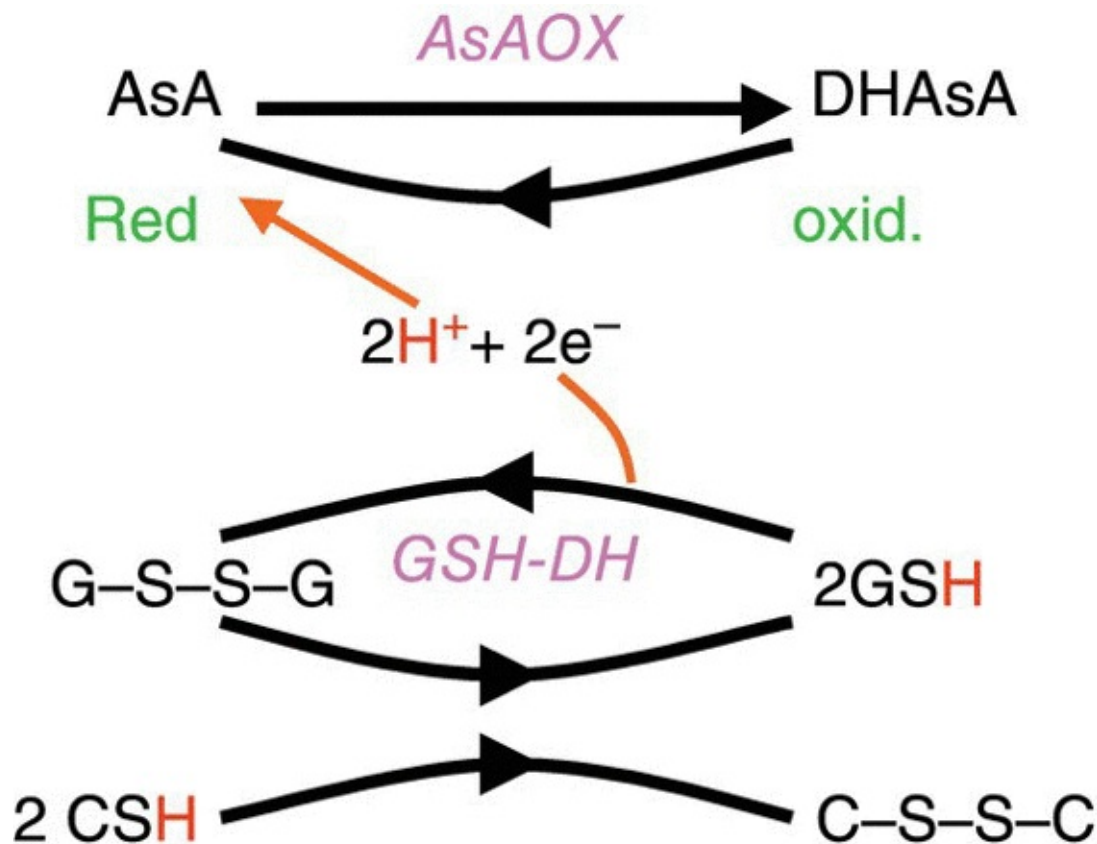
Figure 16.2 The effect of ascorbic acid by reducing the amount of GSH.

Ascorbic acid is a useful oxidant in the production of hearth loaves because activation takes place in the early fermentation process. Ascorbic acid is added to flour in a level of 2–6 g/100 kg flour.

Reducing agents

The major reducing agents are cysteine, l-cysteine, and glutathione. For cysteine, two cysteine molecules in gluten are oxidized and a disulfide bond is built, which causes dough strengthening. Addition of l-cysteine to flour makes dough more extensible and less strong. l-Cysteine will connect with the free glutathiones of gluten and block them, minimizing the effect of oxidizing agents. The advantages of l-cysteine are improved machinability, shorter mixing time, reduced proofing time, and more uniform quality of baked goods.

Reducing agents such as l-cysteine and glutathione are added to doughs to shorten mixing and fermentation time. This is called activated dough development. Reducing agents promote depolymerization of high molecular weight glutenins, which are converted into smaller fragments during mixing. During proofing these fragments are oxidized again to form larger polymers. With activated dough development, extra oxidizing agent is added to promote polymerization, or to strengthen the dough. The concentration used is mostly a premix of 10% l-cysteine with 10% ascorbic acid. l-cysteine opens the disulfide bonds during mixing

(less energy) and ascorbic acid closes the remaining bonds. The added oxidant may not be strong, otherwise cysteine will be oxidized to cystine (dough strengthener). With high-speed mixing, addition of an emulsifier can slow down gluten breakdown.

Addition of cysteine makes gluten less tough, and dough homogeneity improves and fermentation time decreases. Usual doses are between 10 and 30 g 10% l -cysteine/100 kg flour.

Vital gluten

Gluten is a by-product of wheat starch. For economical reasons, more and more wheat starch is produced at the expense of corn starch. As a result, the production of gluten is increased.

With the extraction of gluten, the typical tendency of gluten proteins to aggregate is used. Basically two processes are applied in the production of gluten, starting from wheat flour, namely the "dough" process and the "batter" process. These two processes differ in the ratio of water to flour that is initially mixed, and in further separation of starch fraction and gluten fraction. After washing, the wet gluten is dried so that vitality is preserved.

Vitality is essential for the commercial gluten since their functionality depends on it. Drying of the gluten is probably the most critical step during processing. Drying requires heat, and heat leads to polymerization of glutenins by rearrangement of disulfide bonds, as a result of partial unfolding of the protein structure. There is no longer equilibration between viscoelastic properties of the gluten: the extensibility decreases and the resistance increases relatively. A quality parameter for functionality of gluten is extensibility. Temperatures above 55 °C affect the functionality of gluten.

Hydration capacity and velocity are also considered as criteria for functionality. In modern baking processes that use high-speed mixers, a fast gluten development and interaction with flour proteins essential. That is, the more vital the gluten, the faster it hydrates.

The most important application of gluten is in the bakery sector. Gluten are used to enrich flour that has a lower protein content or weaker viscoelastic properties. Addition of 1–2% vital gluten to native wheat flour can replace a part of expensive imported wheat.

Vital gluten plays an important role in whole-meal flour or bread with an increased quantity of fibers or germs. Addition of 5% or more vital gluten permits whole-meal bread to have a good volume and a better structure and texture.

Other applications of vital gluten are breakfast cereals, pasta products, biscuit rusks, meat products, pet foods, and so on.

The effect of vital gluten on baking behavior is expressed in functional properties:

- improved mixing tolerance,
- increased dough stability during fermentation,
- make-up and final molding,
- increased hydration,
- raised loaf volume,
- improved structure,
- texture and softness of crumb, and
- prolonged shelf-life.

Vital gluten can absorb almost twice its weight in water (140–180% water). The quality of dry vital gluten is estimated with the Brabender farinograph: a comparison among gluten quality, mixing time, and baking performance.

Enzymes

Wheat flour contains a wide range of enzymes, mostly located in aleurone layer and germ. The most important enzymes are amylases, proteases, and oxidoreductases. Enzymes lead to improved dough characteristics, such as increased tolerance, and bigger volume development. The enzyme quantities in flour can fluctuate, so it is important to standardize and optimize the enzyme concentration in flour. One of the main reasons for this is the need to provide sufficient sugars for yeast and gas development.

Amylases

α-Amylase

α-Amylase is an endoenzyme that acts as a catalyst in the hydrolysis of starch. This enzyme is mostly indicated as a liquefier because the viscosity of starch decreases after the action of α-amylase. Originally, malt was the only source of α-amylase for the bakery industry. After the World War II, fungal amylases and bacterial amylases became available. The main difference among the three amylase sources is the heat stability.

Wheat flour contains approximately 0.5% fermentable sugars, which is insufficient for an optimal yeast growth and gas production. A simple solution for this problem is the addition of a sufficient quantity of sugar. However, it is recommended to provide a constant release of sugar for a continuous gas production during fermentation.

In wheat milling, approximately 5 to 10% of the starch in the flour is damaged. Damaged starch is able to absorb a lot of water during dough preparation. These swollen parts of starch granules have a negative effect on mixing characteristics of dough, due to their high viscosity. α-Amylase is able to break down the 'high absorption' parts of the starch and improve the dough. Crust colour and bread aroma are also improved by the impact of α-amylases, by formation of sugars and the resulting Maillard reactions.

When bread is aging, water migrates from crumb to crust. The crumb becomes more firm and loses softness as a result of starch crystallization. This phenomenon is called retrogradation. The clearest characteristics of bread aging are a firm and dry crumb, a soft crust, and the absence of the odor of fresh bread.

Retrogradation of bread can be retarded by different interactions, among which, a controlled hydrolysis of starch by α-amylases is one of the most important. The best effect is reached when only a part of the gelatinized starch is modified (modified starch structures increase moisture retention), and the use of malt or fungal amylases makes this possible.

β-Amylase

β-Amylase is present in wheat flour as a constant quantity, irrespective of the concentration of α-amylase. β-Amylase is an exoenzyme that splits off maltose, starting from the non-reducing end of the starch chain. α- and β-Amylase only attack the α-1,4-glycosidic linkages in starch. This action stops when a branching point, α-1,6 linkage, is reached. Both α- and β-amylase put maltose at the disposal of yeast, which reduces it to fermentable single sugars.

It is common knowledge that wheat flour contains an excess of β-amylase, but attention is

only paid to the addition of the quantity of α-amylase. Research has shown that when the β-amylase content is doubled, dough becomes non-machinable because of stickiness. The reason is difficult to explain, but it is a combination of the action of damaged starch and α- and β-amylases.

Sources of amylases in bakery products

Malt from barley has been used for a long time, especially in the brewery. Barley kernels are soaked and germinated. This green malt is kiln dried and milled to malt flour for use in bakery products as α-amylase source. Amylases from barley malt also contain proteases, which are responsible for weakening gluten proteins. To inhibit the degradation of gluten, barley malt is heated, which inactivate the proteases. The optimal temperature for protease activity is 45–50 °C.

Diastatic malt has only amylase activity. Proteolytic malt also has protease activity and is used in strong flours.

The preparation of wheat malt is comparable to that of barley malt. Wheat malt has less proteolytic activity. The amylase activity is expressed in SKB-units (SKB: Sandstedt, Kneen and Blish) and is between 50 and 150 SKB/g malt flour. Wheat malt flour is usually added in a level of 0.1–0.4%, depending on the amylase activity of the flour. Prior to malt flour addition, amylase activity of flour must be determined (Falling Number method or Brabender amylograph).

Malt syrup is prepared from barley malt by extraction with water. A high amylase activity occurs, and starch is converted to dextrins and sugars. The extract is filtered and concentrated to obtain a viscous product containing amylases, proteases, sugars, and dextrins.

Fungal amylases are preparations produced by molds, such as *Aspergillus oryzae, Aspergillus niger, Rhizopus oryzae*, or *Rhizopus delemar*. Their activity is much stronger than that of malt flour, with less proteolytic effect, and is between 500 and 1000 SKB. At the present time, their activity is mostly expressed in FAU, fungal amylase units. Fungal amylases are not activated by Ca, and their thermal stability is lower than that of malt amylases. Overdosing of fungal amylases is less dangerous than overdosing with malt amylases, and fungal amylases have a bigger effect on dough fermentation between 28 and 30 °C, than malt amylases. Fungal amylases also have another group of active enzymes: gluconases and amyloglucosidases. Gluconases attack starch, limit dextrins, and produce glucose. Amyloglucosidases attack starch, limit dextrins and maltose, and produce glucose. The enzymes are added to give crust more color and flavor, and glucose undergoes Maillard reaction. The amyloglucosidases of *Aspergillus oryzae* are inactivated at 70 °C.

Bacterial amylases are highly active, so they are mostly unfit for use. Amylases from *Bacillus subtilis* and *Bacillus diastaticum* are active during fermentation, gelatinization, and the baking process, and they have a high thermal stability, so they can survive the baking process. Because of their high activity level and thermal stability, it is easy for an excess quantity of starch to be attacked, resulting in a sticky or gummy crumb. Bacterial amylases must be added precisely and in small doses. They are effective in retarding bread firming (Akers and Hoseney 1994), but are not universally used.

Another bacterial amylase source is *Pullularia pullulans*, which can break down pullulan. Pullulan is a polysaccharide consisting of maltotriose units linked by α-1,6 bonds. Pullulanase

is a α-1,6 amylase that is mainly used in the conversion of starch to monosaccharides. Although bacterial α-amylase has a risk in overdosing and excessive hydrolysis of starch, when combined with pullulanase, fewer dextrins are formed, and doughs are less sticky. Pullulanase has no effect on starch retrogradation (Martin and Hoseney 1991).

Proteases

Functionality in bakery products

The quality of wheat flour is mainly associated with the quality and quantity of the proteins in flour. Usually, high protein content is preferred, and the presence of protein-degrading enzymes is considered unpleasant. Addition of proteolytic enzymes to flour is advisable in very few cases. Very strong flours need a supplementation of proteases (mostly fungal) to obtain a certain degradation of the gluten structure. This leads to better machinability of the dough because energy input is less. Loaves also have bigger volumes and crusts without cracks and blisters.

Wheat flours used for the preparation of cookies and crackers have lower protein content, so their doughs should to be soft and extensible. With the addition of proteases, these doughs can reach a higher level of development and produce cookies with more regular, symmetric, and uniform shapes. The optimal dose of proteolytic enzyme is dependent on flour quality, baking conditions, fermentation time, temperature, and mixing method. Excess protease produces doughs that are sticky and slack.

Protease is present in wheat flour in small quantities. Fungal α-amylases contain proteolytic activity, and the risk of overdosing is usually linked to protease content. Today, fungal α-amylases are available with only traces of proteases, as are fungal proteases with few α-amylases.

Sources of proteases in bakery products

Malt proteases hydrolyze gluten proteins and make dough softer. They cause destruction, especially in weak flours. α-Proteases attack gluten proteins, and β-proteases form low molecular peptides.

Aspergillus oryzae is a source of fungal proteases. These proteases contain endopeptidase activity as well as exopeptidase activity. Endopeptidases attack inter-SS-bonds and change the viscoelastic characteristics of dough. Exopeptidases split off end-standing amino acids such as leucine and phenylalanine, which play an important role in color, flavour, and taste of the baked product.

Fungal proteases are less heat resistant than malt proteases: they are inactivated quickly by increasing temperature, so activity is limited to the dough phase.

Bacterial proteases are most active and are used exclusively in the United States, to weaken rusk dough. Bacterial proteases originate from *Bacillus subtilis* and show mainly endopeptidase activity. Bacterial proteases are useful in laminated dough (for crackers) to prevent cracks and curling and gas bubble formation.

Lipases

For a long time, lipase activity in flour has been associated with its deleterious effects on the bread making process. Lipases play a role in the increase of free fatty acids during long-term storage of flour, and have an negative effect on taste and shelf-life. However, the lipase activity of wheat flour is very weak (Castello and others 1998).

Over the past two decades, lipases have been used more frequently. They are added to wheat flour doughs, to improve the characteristics of doughs and baked products. A lot of research has been done on the field of the working mechanisms of lipases. At the present time, lipases work more specific. The second and the third generation lipases work on both polar and non polar lipids in the wheat flour. Lipases hydrolyze triglycerides into mono- and diglycerides and free fatty acids. Lipases increase dough gluten network and dough stability, which increases dough machinability and dough handling properties. Lipases have positive effects on loaf volume and crumb structure. Crumb structure becomes more soft by which lipases work as emulsifiers (Moayedallaie and others 2010).

Enzymes, and thus lipases also, become denatured during baking and become undetectable in the final product. This give enzymes the opportunity to be clean label improvers. Lipases are more and more used as a replacer of emulsifiers. Lipases are also more cost-effective than emulsifiers (Moayedallaie and others 2010).

Lipoxidases

Lipoxidases catalyze the oxidation of unsaturated fatty acids and carotene pigments of flour by bleaching them. Flour of soybeans and other leguminous seeds contain lipoxidases and has been added for many years as a flour improver. Lipoxidase acts specifically and attacks only linoleic, linolenic, and arachidonic acids and their esters: only the configuration cis,cis-1,4-pentadiene is attacked (Pyler 1973).

Endoxylanases

Wheat flour contains approximately 3% non-starch polysaccharides. Arabinoxylans are responsible for 85% of these polysaccharides. Only 25–30% of the 1.5–2.5% arabinoxylans in wheat flour are water-extractable. The water-unextractable fraction can be treated with alkali, which makes a large part of the molecules water soluble. Also, enzyme treatment with endoxylanase results in solubilization by hydrolysis of the xylan backbone.

Formerly, the so-called pentosans were mentioned in literature on bread making. At the present time, research has led to better knowledge and to a distinction between arabinoxylans and arabinogalactanpeptides, another class of non-starch polysaccharides in wheat flour. The two molecules differ in structure and properties. Thus, the term *pentosans* is no longer used.

Arabinoxylans consist mainly of arabinose and xylose. Arabinoxylans can absorb several times their weight in water: 3–6 times for the water-extractable fraction, 6–10 times for the water-unextractable fraction.

Another important characteristic is their ability to cross-link and to gel under oxidizing conditions. The main result of oxidative cross-linking is a strong increase in the viscosity of arabinoxylans in solution. When the arabinoxylan concentration is sufficiently high, a gel is formed. In the bread making process, arabinoxylans are responsible for a higher dough consistency and increased dough development time.

Endoxylanases, whose activity level in wheat flour is low, have a strong impact on arabinoxylan structure and functionality. They attack the arabinoxylan backbone in a random manner. Endoxylanases have also been found in bacteria, fungi, insects, and elsewhere and have been selected according to their functionality: selectivity, stability, temperature, and pH activity range.

Addition of endoxylanases in an optimal dose decreases dough stiffness and dryness and increases dough elasticity, extensibility, and coherency. Endoxylanases have an improving effect, especially on poor quality flours. Overdosing destroys the water binding capacity of the arabinoxylans and results in dough stickiness.

During fermentation and oven spring the water-extractable arabinoxylans increase the stability of the liquid films and of the foam structure of the dough by increasing the viscosity of the dough aqueous phase. The water-unextractable arabinoxylans have a negative effect on bread quality. Addition of endoxylanases with the selectivity for the water-unextractable arabinoxylans helps solubilize them, resulting in improved gas retention, increased oven spring and loaf volume, and improved crumb structure (Courtin and Delcour 2002).

Emulsifiers

For the last half century, emulsifiers and surfactants has been successfully used in the baking industry. The large-scale production and mechanization in the bread making process and the increased consumer demand for high quality, convenience, and longer shelf-life have created the need for functional food additives such as emulsifiers to achieve those aims.

Definition

Emulsifiers belong to the general class of surface-active agents and are able to form an emulsion with two liquids that are normally immiscible. Emulsifiers and surfactants are fatty substances containing both lipophilic and hydrophilic properties.

Food emulsifiers can be classified on the basis of several characteristics including origin (synthetic or natural), solubility properties, the presence of functional groups, hydrophilic–lipophilic balance (HLB), and potential for ionization (non-ionic versus ionic).

For the baking industry, many characteristics are expected of emulsifiers: improved dough handling properties; improved rate of hydration and water absorption; greater tolerance to resting time, shock and fermentation; improved crumb structure (finer and closer grain, brighter crumb, increased uniformity in cell size); emulsification of fats and reduction of shortening; improved gas retention, better oven spring, increased loaf volume; and longer bread shelf-life (Stampfli and Nersten 1995).

Functionality of emulsifiers

The effect of emulsifiers is situated on starch and gluten proteins. The interaction with starch produces softness and shelf-life; interaction with gluten proteins is emulsification and fat distribution, resulting in better volume, stability, and structure.

Crumb softeners

Crumb softeners are emulsifiers or surfactants that interact with starch and thereby retard staling. These emulsifiers are able to form complexes with amylase that are insoluble in water. The part of amylose that is complexed, for example, by monoglycerides, does not participate in the gelatinization process during baking, so less water is absorbed by starch and more is available for gluten proteins. Therefore, upon cooling, the complexed amylose will not recrystallize and will not contribute to staling of the crumb (Stampfli and Nersten 1995).

Interaction of emulsifiers with amylopectin blocks the side chains of amylopectin, thus retarding retrogradation.

Dough conditioners

A scientific explanation for loaf volume increase and improved crumb structure due to emulsifiers can't be given, but one theory is the emulsification or lubricating effect: Flour, water, salt, and yeast are mixed into a complex dough, consisting of starch that is held together by gluten strands together with the water. These gluten strands form a network. Adding fat to the dough will decrease the friction between the gluten strands themselves and

between gluten strands and starch particles, resulting in improved viscoelastic properties of the dough. The dough has a better machinability, and results in a finer crumb grain. At the same time, the fat that is absorbed by the gluten strands makes them more supple. Both effects contribute to improve gas retention. An emulsifier provides good emulsification of fat in dough and dispersion of the fat as a film between gluten strands and starch particles. The unstable starch-water-suspension becomes stabilized as the hydrated starch granules repel each other. All these effects give a good "conditioned" dough or "strengthened" dough, which results in a bigger loaf volume, a fine and regular crumb structure and crumb grain, and softer bread.

Emulsifiers in the baking industry

A wide range of emulsifiers is used in the baking industry, although only a few are really emulsifiers. Most of them are surfactants that have the same effect on baking quality. The major differentiation is between crumb softeners, which improve softness of baked products, and dough conditioners, which improve dough properties.

Lecithin

Lecithin is a real emulsifier and was the first emulsifier used is the bakery industry. It is a natural product extracted from soy or corn oil. Commercial lecithin contains half or more of the oil from which it is extracted from and pure lecithin. It is a plastic substance that is easy to process in bread doughs. Powdery lecithin is also made up of approximately half pure lecithin.

Lecithin belongs to the polar phospholipids and contains glycerol with two fatty acid groups and a phosphate group on which choline is bound. The phosphate group in combination with the fatty acid groups gives lecithin the typical properties of an emulsifier. Figure 16.3 shows the structure of lecithin.

$$OCH_2 \longrightarrow COR_1$$

$$OCH \longrightarrow COR_2$$

$$OCH_2 \longrightarrow \underset{OH}{\overset{O}{\underset{|}{\overset{\|}{P}}}} \longrightarrow OCH_2CH_2N(CH_3)_3$$
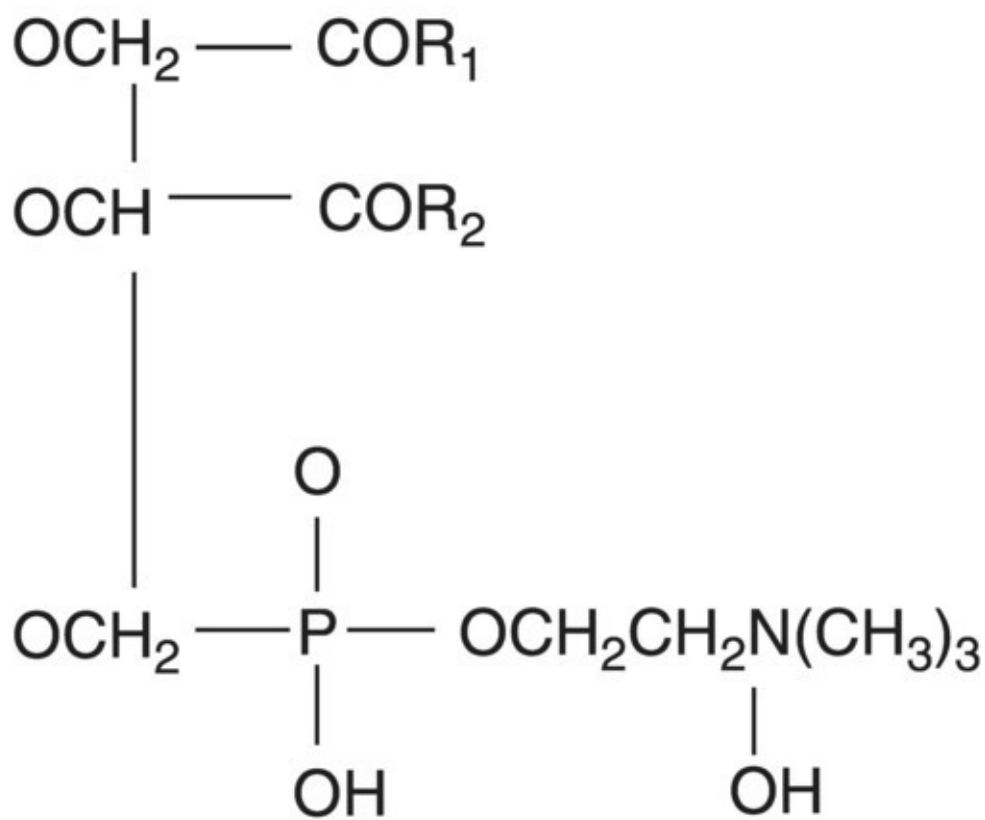
Figure 16.3 Formula of lecithin.

A lot of combinations of R_1 and R_2 are possible. This non-polar side chain has a pronounced lipophilic character due to two relative long carbon chains (Garti 1999). P-choline is polar.

Commercial products from corn or soy contain also other emulsifiers. Soy contains 31% cephalin, 40% phosphatidyl inositol, and 29% real lecithin.

Pure lecithin is insoluble in water; it must first be made soluble in oil. The hydrophilic character of lecithin can be increased by treatment with hydrogen peroxide and lactic acid.

The effect of the addition of lecithin expresses itself in a finer crumb grain, greater loaf volume, better gluten stability, better emulsification of fats, longer shelf-life, and increased water hydration. Normally, lecithin is used in the preparation of darker breads and mixed grain breads. Lecithin has the most effect on flours of weak wheat, especially with milling yields of 85–100%. Addition of 0.2% pure lecithin (relative to flour base) gives the maximal improvement possible, depending on the flour quality. Higher additions result in decreasing volume, minor crumb structure, and crumb softness.

The effect of lecithin is due to its surface active and emulsifying properties. It also reacts directly with flour in the following stages: physical adsorption on the surface of flour particles, swelling and formation of chemical linkages, and condensation to lipoproteins. The decisive reaction is obviously the formation of the lipoprotein complex. This strengthens the protein structure of the dough. The gluten becomes more elastic and smoother, gas retention is improved. In addition, retrogradation of starch is inhibited and shelf-life is extended (Spicher and Brümmer 1995).

Monoglycerides

One of the most common emulsifiers for water-in-oil emulsions is monoglycerides of fatty acids. When hydrogenated oils or natural fats are transesterified with glycerol, the result is a

mixture of mono- and diesters of fatty acids. Upon further treatment (purification by extraction or molecular distillation), relatively pure alpha-monoglyceride esters (at least 92%) can be prepared (Garti, 1999).

Mono- and diglycerides, originating from unsaturated fatty acids, are weak and plastic and can be added to dough as such. If they are built up from saturated fatty acids, their consistency is rather wax-like. On the other hand, monoglycerides from unsaturated fatty acids are less effective as an improver.

In the baking industry the monoglycerides from saturated fatty acids are mostly applied, as powder, as flakes, or dispersed in vegetable oils.

Glyceryl monostearate (E 471) is in the first place a crumb softener, and is not effective as a powder, because it does not dissolve in the dough water. Glyceryl monostearate (Figure 16.4) is used as a bread improver and must be emulsified in water before it is added to dough. Glyceryl monostearate has a HLB value of 3.8 (Spicher and Brümmer 1995). Glyceryl monostearate has the greatest effect on softness, and less effect on loaf volume. The result is a fine crumb with considerable elasticity. The action of glyceryl monostearate is based on retarding starch retrogradation. Optimal dosage is 0.2% relative to flour base.

$$CH_2-OH$$
$$CH_2-OH$$
$$H_2C-O-CO-(CH_2)_{16}-CH_3$$
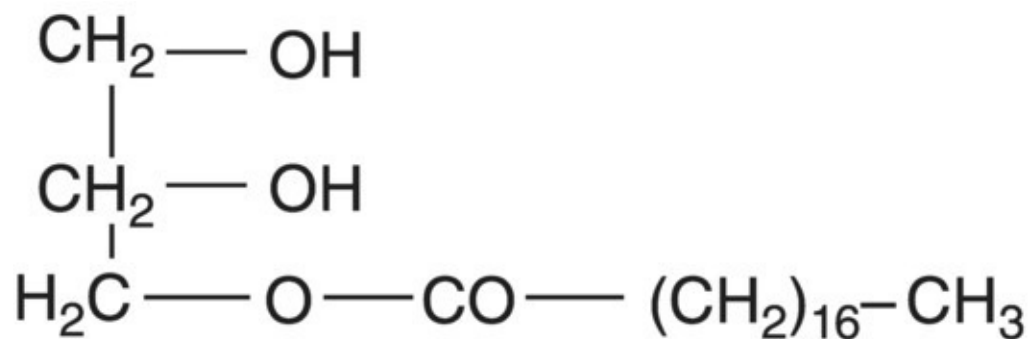
Figure 16.4 Formula of glyceryl monostearate.

Calcium stearoyl-2-lactylate

Calcium stearoyl-2-lactylate (E 481) is a typical dough conditioner with a HLB value of 8 -10. The anionic stearoyl lactylates are esters of lactic acid and fatty acids, usually partially neutralized in the form of calcium stearoyl-2-lactylate (CSL) or sodium stearoyl-2-lactylate (SSL). The fatty acids esterified to the polar group may be blends with chain lengths from C_{12} to C_{20}, depending on the type of hydrogenated or unhydrogenated fat (edible lard or tallow, sunflower oil, soy bean oil, etc.) or fatty acids used in the manufacture of surfactants. Both the fatty acid chain length and the degree of unsaturation are important for the functional properties of the surfactants (Krog 1981).

CSL is not an emulsifier but a surfactant, and it is an excellent product in bakery goods: volume, baking behavior, crumb grain, and softness are favorably affected. Crumb structure especially becomes finer and more uniform. Shelf-life is extended, and the machinability of the dough is improved.

CSL (Figure 16.5) is commonly used in the manufacture of white bread. Optimal dosage is 0.25–0.50% on a flour basis.

Figure 16.5 Formula of calcium stearoyl-2-lactylate.

SSL or sodium stearoyl-2-lactylate is dissolvable in water and shows properties for both dough strengthening and crumb softening (Stampfli and Nersten 1995). It is widely used in the bakery industry, especially for the production of cakes.

Diacetyl tartaric acid esters

Diacetyl tartaric acid ester, or DATA, is prepared by reaction of acetic acid anhydride and tartaric acid with mono- and diglycerides. In fact, DATA is a mixture of different diacetyl tartaric acid esters. The composition of the end product depends on the ratio and composition of the raw materials and reaction conditions. The structure of DATA is shown in Figure 16.6.

Figure 16.6 Formula of diacetyl tartaric acid ester.

Depending on the R-groups DATA (also called TEM or E472) may be liquid, plastic, or solid at room temperature. The product has a typical acetic acid smell and taste, and the HLB value is 8–10. Legally, a maximum of 1% of DATA in flour is tolerated. The optimal dosage is between 0.25 and 0.50%. DATA has an additional effect on oxidizing agents such as ascorbic acid.

DATA has a strong improving effect on loaf volume and dough stability. To a lesser extent, crumb structure is improved, but it becomes more uniform. Crumb grain becomes rather coarse, with a tendency to holes with weak flours. This tendency makes DATA suitable as a bread improver for crusty breads. It can also be used in white breads to get an open crumb grain.

Hydrocolloids

Hydrocolloids are widely used in the food industry because they modify the rheology and

texture of aqueous systems. Hydrocolloids affect the stabilization of emulsions, suspensions, and foams, and modify starch gelatinization.

In the baking industry hydrocolloids are of increasing importance as bread making improvers. They improve dough-handling properties, improve the quality of fresh bread, and extend the shelf-life of stored bread (Rosell and others 2001).

Hydrocolloids, such as carboxymethylcellulose (CMC) and guar gum, have proven their benefit in the formulation of gluten-free breads. Sodium alginate, κ-carrageenan, xanthan gum, and hydroxypropylmethylcellulose (HPMC) improve wheat dough stability during proofing. Addition of xanthan gum in frozen dough has the ability to increase the dough's stability during freeze–thaw cycles (Guarda and others 2004).

CMC and HPMC have a combined effect with enzymes and emulsifiers on textural properties of both dough and fresh bread, for example, high volume and retarding of staling (Collar and others 1999; Rosell and others 2001; Guarda and others 2004).

Hydrocolloids must be used in small quantities (< 1% on flour base) and are expected to increase water retention and loaf volume and decrease firmness and starch retrogradation (Collar and others 1999).

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Part 4
Baking Science and Technology

17

Mixing, Dough Making, and Dough Make-up

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Introduction

The first stage in dough processing is mixing. During mixing both the development of the dough and the temperature of the dough are established. If one or both is not achieved during the process, the product quality will suffer.

It cannot be stressed enough that mixing is the most important stage of the entire baking process. If it is not done properly, it is not possible to correct it later. Therefore discipline is required. It is not easy to repeat exactly the same process every 12 or 15 minutes; however, it is necessary and of the utmost importance. Someone who wants to be proud of the quality of the product he has made must also be proud of the fact that he is capable of repeating the same process over and over again – and that is a real challenge.

Mixing process

Scaling of ingredients

Another aspect of the process is that all ingredients must be correctly weighed and that all ingredients should be added to the dough. An easy method to check whether there is yeast in the dough or not is to put a little piece of dough in lukewarm water. After a while it should start floating because CO_2 is produced, which changes the specific weight of the dough. The dough becomes lighter so it begins to float in the water.

Tastinge a little piece of dough will establish whether or not the salt has been added. The yeast must not be allowed to come into direct contact with the sugar, or especially, the salt. Because of its hygroscopic nature, the salt will start to move water out of the yeast cell (osmotic pressure) and the yeast will dehydrate, a process that can be compared with a grape becoming a raisin. If salt is put on the yeast, it will start to dissolve and the mixture will start to liquefy.

Objectives of the mixing phase

Most of the characteristics of the final product are determined directly or indirectly during the mixing stage. Undermixing or overmixing the dough will affect its handling properties. Scaling is very important as incorrect scaling of the ingredients will result in various faults in the bread, depending on which ingredient is weighed incorrectly. The dough temperature is also crucial so that the correct fermentation rate is achieved, which will influence the volume of the bread and the color of the crust. Finally, the duration of mixing must be correct or the texture and the grain of the crumb will be wrong.

Dough mixing has a number of objectives:

- to uniformly incorporate all ingredients,
- to hydrate the flour and the other dry ingredients, and
- to develop the gluten.

An input energy is required to mix the water and flour and thus slowly develop the gluten network. The art is to obtain the proper consistency so the dough will have excellent machinability as well as good gas retention properties.

Mixing time

In a conventional spiral mixer, the mixing time for a dough of about 165 kg will be around 12 min, depending on such factors as the quality of the flour and the mixing method (for example, when the salt is added will influence the mixing time; delayed salt addition shortens the mixing time).

During this 12 min, a number of stages can be distinguished:

- *pick up*: the dough is sticky, cold and lumpy;
- *initial development*: the dough is getting warmer, smoother and drier;

- *clean up*: the dough is at maximum stiffness and comes together as one mass. The color will change from yellowish to a whiter, creamy colour;
- *final development*: the dough is at its correct temperature and handling quality. A gluten film can be easily obtained by stretching a piece of dough.
- *letdown*: the dough is too warm and becomes sticky, lacks elasticity and has too much flow;
- *breakdown*: the dough will begin to liquefy.

The mixing time is influenced by a many factors, including:

- the speed of the mixer,
- mixer design,
- dough size in relation to mixer capacity,
- dough temperature,
- the efficiency of the cooling systems,
- the quality of the flour,
- water absorption of the flour (influenced by the particle size),
- amount of shortening – mixing times increase with more added shortening,
- amount and type of reducing and oxidizing agents,
- amount of milk solids and other dry ingredients that compete for the water – the higher their concentration is, the longer the mixing time will be because there is less water available for gluten development.

Types of mixers

There are several different types of mixers. Blending and dough break is relatively unknown, but it is a very interesting technology. Dough break is still used quite often in Italy to make typical Italian bread rolls. After mixing, the dough is run through rollers again and again in order to get a very, very fine structure. It is also used in automatic lines for toast bread. Other better known mixer types are the spiral mixer, the fork mixer (typically used for baguettes), the artofex mixer (mimicking the movement of human arms), and the vertical mixer (Hobart type with dough hook). The horizontal mixer is seldom found in Europe, but is very popular in the United States. Others are the high-speed mixer (with or without the possibility of applying a vacuum during mixing) and the continuous mixer (Stear 1990).

In Europe, horizontal mixers have not been very successful. Instead there have been several vertical technologies applied to machine mixing of doughs, until recently often varying by country more than by product. Two traditional technologies that have retained some degree of relevance up to the present day are twin-arm mixing and fork mixing, especially within their respective niches. In any case, somewhat of a revolution was begun in Europe about 30 years ago with the invention of the spiral mixer, now the most successful of the various vertical technologies. The spiral kneads the dough very naturally and efficiently by pushing and stretching the dough against the bowl surface as it moves past the spiral tool. It has

several general advantages over other technologies, and since its introduction has rapidly overtaken all other European mixing technologies in popularity, due to its higher speed, efficiency, and adaptability to a wide range of product types. Certain factors mentioned later have, until now, limited the acceptance of spiral mixers within industrial settings in North America, and while not all spiral mixers are created equal, in general the quality and efficiency of dough development produced by this technology is undisputed.

Horizontal mixing has remained the standard for dough operations in the United States, which has resisted the influence of the spiral mixer for various reasons. For example, the early mixers imported from Europe were not mechanically up to the stress of working with American flour, with its high protein content and correspondingly high torque demand. Spiral tools snapped, shafts broke, bowls came off their supports, and motors died. It was enough to disillusion any serious manufacturer. Also, higher production levels in the United States demanded larger batches than those historically available with vertical mixers. Even when capacity was not an issue, time was. Spiral mixers typically mix more quickly than horizontals. Smaller more frequent batches require more frequent scaling of ingredients; if automation is not used, this implies additional labor and an additional opportunity for mistakes. Finally, though heat rise is generally lower with spiral mixers, cooling can still be an issue, and since manufacturers have not worked out a good way to jacket a rotating spiral mixer bowl, alternatives – such as CO_2 injection (which can be expensive) or cooling of the primary ingredients – have to be considered for dough temperature control. As well as this, there has been simple force of habit, suspicion of non-American technology, and existing investment in dough troughs and other incompatible design elements. Taking all this into consideration, most US companies have continued to use horizontal systems.

More than 15 years ago, European companies began to address these issues in a completely different way from their American counterparts. Automated bowl handling systems began to appear that could completely automate the vertical mixing process without sacrificing either the mix quality or the preference for more frequent batches. The first of these to appear, the carousel system, places the mixing bowls on a turntable, rotating the bowls between the various stations (ingredient feeding, mixing, resting, if any, and discharging). Later, linear systems, sometimes referred to as robot systems, arose that had the advantage of a flexible cycle allowing, for example, production of both doughs requiring rest time and those that are processed straight through. Perhaps most importantly, they retained the flexibility to make future products with mixing cycles not defined or even imagined at the time of initial purchase. Carousel systems and robot systems could be fitted with any type of vertical mixer that would work with a product, such as twin-arm mixers for pie doughs or other doughs in which it was vital that no heat be gained. An example is a system composed of four carousels processing 4800 lbs of pie dough. French fork mixers for baguettes, spiral mixers for bread and pizza, and so on, will also work with vertical mixers. Development of even higher speed vertical systems, including twin-spiral technology, allowed for much higher production rates from vertical mixers and further helped open up the possibility of using these systems at the highest industrial levels. At present, if you tour a European bakery, you are likely to see one of these systems mixing away, with one operator, or sometimes no operator at all, continuously providing the make-up line with dough.

How does one decide between a carousel and a robot, or linear carousel, solution? Basically the issue is one of flexibility. The carousel system is typically the more efficient in terms of

purchase cost versus productivity. This is mainly due to the very minimal dead time in the system. The downside is that the cycle is fixed. Each product will move from one station to the next in the same order as the others. With additional mixing heads, ingredient feeding stations, and additional resting positions, carousels can get somewhat complicated and allow for a certain degree of flexibility. Two examples can be considered: (i) the system for baguette production operating in the United States, which incorporates two different production cycles; (ii) for extreme products, like the Italian panettone, which requires a process that takes more than 30 h from start to finish, several carousels can be linked, forming a very complex process. Nevertheless, there is an inherent rigidity to carousel design.

A linear carousel, or robot, on the other hand, offers greater freedom because the shuttle that moves the bowls operates much as a person would, taking a bowl from one position and depositing it in another. With today's sophisticated controls, it is simple to simultaneously produce some product recipes that call for floor time and others that don't.

Whatever type of mixer or system is used, remember that the principal aim is always the same, to develop the gluten to maximum gas retention capability. Remember also that the type of mixer, together with other mechanical actions, will influence the changes dough will undergo during rounding and molding – the final structure of the crumb. And, furthermore, that final structure will influence the eating characteristics, the softness and color of the crumb, the staling, the volume, and other important qualitative aspects of the final product (Dobraszczyk and Morgenstern 2003).

Chemical aspects of dough mixing: oxidation and reduction

High-speed mixers are being employed with ever increasing numbers in manufacturing allowing short-time doughs to be fully developed in less than 5 min and thus addressing the problem of meeting mixer schedules with a dough system that generally requires more mechanical development.

One version of a high-speed batch mixer can mix bread doughs in just 3–5 min. The mixer uses a mixer arm that turns at 1750 rpm (revolutions per minute), mixes in a sealed chamber and can be tied into a programmable microprocessor for a complete computerized mixing operation.

Computerized ingredient handling (see the section in this chapter on Automating the mixing room), including scaling of ingredients, now makes it possible to handle in bulk no-time dough concentrates and bases with automated scaling, which was until recently used exclusively for major ingredients.

Much work is needed on controlled-atmosphere mixing for dough development. Recent experiments on controlled-atmosphere mixing suggest that by controlling the type of gas blanket dough is mixed in, the baker may be able to reduce or eliminate the addition of maturation ingredients to doughs.

As necessity is certainly the mother of invention, pressure to meet increasing demands for efficiency, for cost reductions in both labor and processing, for improvements in product quality, and of an ever-changing marketplace will continue to stimulate everyone to modernize bakery operations, including short-time fermentation systems.

Oxidation of the dough

The molecular entity that gives dough its cohesiveness and structure is gluten. Gluten is a tightly coiled protein that, like many other naturally occurring fibrous substances, contains a substantial number of disulfide bonds. Disulfide bonds are nature's means of giving fibrous structures strength and rigidity. One can compare these bonds to the cross-elements in a ladder or steel structure.

For the dough to rise, gluten must be relaxed; that is, the disulfide bonds must be broken. The mechanical energy imparted to the dough during mixing or dough development breaks these bonds by reduction and results in the uncoiling of the gluten molecule. Sulfhydryl (-SH) groups are formed from the sulfur of the broken linkages, and the dough is free to rise or increase in volume. To maintain this new expanded "structure", the chemistry must be reversed to provide new linkages, that is, the sulfhydryl groups must be oxidized to form new disulfide bonds. This oxidation locks the new "structure" in place.

Oxygen is needed for the oxidation reaction. This oxygen comes partially from the air which is beaten into the dough, but can also be provided by oxidizing agents such as ascorbic acid (which becomes an oxidizing agent when it is transformed into dehydroascorbic acid) or calcium peroxide (Stear 1990).

The function of the oxidizing agent is to oxidize the sulfhydryl groups to disulfide bonds and strengthen the dough. The result is a tightly cross-linked protein structure that, following

leavening, maintains a volume many times that of the original dough. Due in part to the increased strength of the gluten given by the high degree of cross-linking achieved, the dough is drier and less sticky, that is, provides improved machinability. In addition, less dusting flour is required, resulting in fewer streaks and cores in the bread. The decrease in stickiness is particularly important in highly mechanized, high-speed production lines.

After the gluten is mechanically uncoiled, oxidation (promoted by an oxidizing agent) helps maintain the volume gains made during the expansion of the dough by the fermentation process. The expanded dough is able to retain more permanent moisture in the final product; the extra water becomes bound within the dough structure and does not bake out of the final product. Increased water absorption results in softer, more pliable dough with improved texture. The subsequent increases in flour yield compensates for the additional cost of the oxidizing agent.

No-time doughs

At the beginning of their practical application, no-time doughs were a method for producing breads when baked products were in short supply and the time required for baked breads from the sponge-dough process or straight-dough method could not meet market demands. Straight doughs were made with double the normal amount of yeast to reduce the fermentation time to a minimum. The resulting breads were saleable, but flavor was lacking and shelf-life was limited. Bread quality was thought to be less than desired, and short-time ferment systems were, as mentioned earlier, an emergency method of bread production

No-time dough systems are currently much more than an emergency system for dough production. It is safe to say that most retail bakers and manufacturers of hearth-type variety breads, as well as manufacturers of dough for freezing, use no-time or short-time ferment systems. The reason for choosing a short-time ferment system is simple: time savings. In addition, equipment and space requirements are less with the short-time system, and scheduling is simplified. For frozen dough operations, short-time ferment systems are also the best system for achieving product quality and freezer stability.

Short-time ferment systems encompass a wide variety of methods from the simple to complex. Bakers now have at their disposal simple, preblended, short-time ferment concentrates to which the baker must add only topping flour, water, and yeast for ingredients. More complex systems include liquid or preferments, high-speed mixers, and ingredients such as L-cysteine, proteolytic enzymes, oxidants, emulsifiers, and a multitude of dough conditioners, many of which are part of the preblended concentrates. Today's use of the wide variety of no-time dough systems is due to an evolutionary process of continuous experimentation, ingredient and equipment development, and market demands. To better understand where we are today in the use of no-time dough processes, we need to understand these individual important components.

Reducing agents

The use of reducing agents can be a very important economic tool for the baker, because as the need to increase production rates grows, the use of reducing agents decreases the mixing time in a batch-process mixer, and the speed and/or dwell time necessary in the developer head in continuous mixing processes, thus allowing more dough to be processed in a shorter

length of time. It follows, then, that the use of reducing agents substantially reduces the mixing requirements of the dough, and the production rate can be increased further (Kulp 1988).

L-Cysteine

Early in the 1950s, a dairy food processing company began marketing a whey L-cysteine blend of dough conditioner that would change the way bakers view and use no-time dough systems. Using combination whey and L-cysteine allowed bakers to uniformly control rapid dough development to produce consistent quality bakery foods. L-Cysteine is a reducing agent used to reduce the mechanical development required by yeast-raised doughs and to develop the gluten network for proper gas retention. Basically, L-cysteine works by breaking the disulfide bonds cross-linking gluten strands changing them to sulfhydryl bonds. The breaking of the cross-link is considered a weakening effect and will allow the gluten to become more extensible. L-Cysteine begins to work in the mixing stage of the dough development process and will continue to work until the dough is subjected to high heat during the baking process. L-Cysteine reduces mixing time required by the same mechanism, to achieve fully mechanically developed dough with less mechanical input. The greater the level of L-cysteine added to the dough, the shorter the mixing time required – with normal addition to yeast leavened doughs in the range of 25–50 ppm (parts per million) (Stear 1990).

Although L-cysteine reduces mechanical dough development requirements and yields more extensible doughs, it also has negative side effects. The drawback of using L-cysteine is its weakening effect on gluten, which can result in negative finished loaf characteristics such as lower volume, dense grain, and poor eating qualities. L-Cysteine can also affect the flour's tolerance to stresses in mixing and make-up processing, and determining the correct amount of L-cysteine can be difficult as doughs have little tolerance for higher than correct levels so its use requires care in formulation, scaling, and processing. As will be discussed later, some recent research points to the desirability of eliminating L-cysteine from short-time formulations because of the negative effects on dough handling and finished baked food quality. Along with the use of L-cysteine as a chemical replacement for dough mechanical development, other ingredients are necessary to balance the effect of L-cysteine and to chemically replace or accelerate biochemical dough activities that were common in a straight or sponge-and-dough system, but are not effective during short fermentation times.

Sorbic acid

Recently, sorbic acid has gained wide acceptance as a new reducing agent for batch mixed doughs, both for reducing mixing time and as a dough-relaxing agent. Sorbic acid is a proven agent for reducing mixing time for both yeast-leavened and chemically-leavened doughs when it is added at a level of 100–2000 ppm (flour basis). Recommended levels for yeast-leavened products are at the lower end of this range.

The actual chemical changes caused by sorbic acid are not as yet well defined, but the obvious benefits to the baker are a 20–30% reduction in mixing time, a drier, more pliable dough, which does not shrink after going through the sheeter, better pan flow, particularly with hamburger buns, less gassy dough for degassers and extruders, and a finer texture in the finished bakery food.

Sorbic acid is effective in any dough system involving a kneading action in the presence of air.

These processes include the sponge-dough batch process, straight-dough process, and preferment systems using batch mixing. Because of a kneading action is required, sorbic acid is less effective in continuous mixing systems. Sorbic acid is effective wherever it is added, either to the sponge or dough in the batch system, to the dough in the straight-dough system, or to the preferment or dough in the preferment system. It should be noted, at this point, that the low level of use of these reducing agents, in the parts per million range, precludes their use in the concentrated form by most bakers. Products are available in convenient forms that make scaling a practicality for the average baker, and these forms are recommended.

Oxidizing agents

Overview

The role of oxidation is important in the process of all yeast-raised dough manufacturing, but is even more important to the baker in a short-time ferment system because the baker, himself, must control the oxidant and oxidant type. Because of the lack of time in processing, the baker must now, for the first time, be keenly aware of the use and effects of oxidation in the dough system. The effect of oxidation on unleavened dough systems is basically to strengthen the dough system at various critical points in the manufacturing process. The critical points are after mixing for recovery of the dough from mechanical abuse, in the make-up stage for proper machining of the dough, and during the late stage of proofing and early stage of baking for proper gas retention, all of which contribute to proper finished baked product characteristics and quality. The level of oxidation ingredients added is normally greater with short-time ferment systems than with sponge or straight-dough systems. As processing time is reduced, the need for added oxidation will generally increase. Oxidants can be categorized into two groups: (i) early or fast acting, and (ii) late or slow acting.

Early-acting agents such as azodicarbonamide, potassium iodate, ascorbic acid, and calcium peroxide take effect in the mixing and make-up stages of production. Late-acting agents (potassium bromate, calcium bromate) take effect in the proofing and early baking stages and are triggered by heat and low pH. A balance of early- and late-acting oxidation is critical for processing and for the quality of the finished baked goods. Equally important are the type and balance of early-acting oxidation. Normally, a blend of two or more early-acting oxidants is used along with potassium bromate to meet oxidation requirements. The action of oxidation in yeast-raised dough processing is the reverse of the action of the L-cysteine reduction process.

Oxidants react to form or reform the cross-links of the gluten strands, forming disulfide groups, which act to strengthen the gluten strands and dough system for proper gas retention, volume, and characteristics of the finished baked foods. Again, the proper use of oxidation in all dough systems, especially no-time or short-time ferment systems, is very critical. It is well-known that the required amount of oxidants added by the baker depends on the fermentation time and the level of yeast in the dough system, with oxidant additions increasing with a reduction in ferment time and reduced yeast levels (Stear 1990).

Ascorbic acid

Ascorbic acid is generally recognized as safe and has low toxicity: it has been used by physicians as a detoxifying agent in drug poisoning. The amount added to flour for the

desired mixing-speed effect is so small that it has no effect on the dietary requirements of humans. Very little or virtually no vitamin C activity is retained in baked bread, because it decomposes at higher temperatures. Only about 10% survives baking. Ascorbic acid can be used up to 200 ppm (flour basis).

Yeast–oxidation interaction

Yeast, or the reaction of yeast in yeast-leavened dough, seems to act synergistically with oxidation, and minimum fermentation (as little as 15 min) can improve finished loaf qualities and reduce oxidation needs. Higher yeast levels seem to reduce the levels of oxidation added by the baker. It has been found that doughs fermented for 45 min required six times the level of oxidation, specifically potassium bromate, than that of the control straight dough fermented for 3 h (Finney and others 1976).

Recent research at both Kansas State University and the American Institute of Baking have focused on the interaction of yeast with oxidants and the interaction of various types of oxidant in yeast-leavened dough systems. Potassium iodate was found to be beneficial in reversing the reduction effects of L-cysteine in a short-time dough system at levels of 20 ppm. With increasing potassium iodate levels to 30 ppm, lower finished loaf volume was recorded, indicating both that additions of iodate in short-time ferment systems containing L-cysteine are beneficial and that addition of the correct amount is critical.

Automating the mixing room

Batch mixers have been used for many years in the baking industry, and there are several thousand units presently in operation. Mostly, they are tended by one or more operators who not only operate the mixer itself, but also are involved with ingredient preparation and the feeding of the make-up equipment.

Comparing a dough mixer used earlier last century with one in use today, it becomes clear that the underlying mixing mechanics have changed very little. What *has* changed radically is the level of automation and the level of control that we have over the process.

There is a challenge to automate not only the ingredient handling area but also the mixing function. Although the types of dough to be mixed vary greatly, the challenges of automation apply equally well.

The challenges encountered in the mixing room are to (i) reduce or eliminate the mixing room personnel, (ii) minimize the tasks of the mixing room personnel, (iii) maintain or improve product quality with no formulation changes, (iv) ensure the consistency of product from batch to batch, (v) produce products having different recipes, and (vi) to accomplish points (i)–(v) with proven and reliable conventional mixing technology.

Thus, the challenge is to obtain the highest level of automation while ensuring consistent product quality. To do this, it is desirable to automate not only the mixing, but also the feed system of the ingredients and the feed of the make-up equipment. Additionally, continuous and reliable temperature control is essential.

To control these systems and at the same time provide the flexibility needed to handle a variety of recipes, mixing times, and batch sizes, dough must be delivered to the make-up equipment so that the make-up equipment is neither starved nor choked. Monitoring and controlling the entire operation are of the utmost importance. This control is best achieved using a computer, which interfaces with microprocessors on the production equipment.

Manageable and versatile control of an automated mixing system is best achieved using a mainframe, mini- or microcomputer interfacing with the ingredient system and mixer via a programmable controller (PC). The system normally has a flow diagram, which depicts an automated ingredient and mixer system, and shows the relationships and interfaces between the ingredient feed system and the mixer, the make-up equipment, and the computer via a "slave" programmable controller.

What is the role of the computer? The computer stores recipes and ingredient tolerances. It stores inventory data for usage records and reorder purposes. It also stores and prints out production data, such as batch numbers, batch weight (including each ingredient by weight) and batch temperature. The computer is used to make changes to recipes, mixing times, and temperatures. The computer controls and monitors the production equipment via the programmable controller. The computer does not perform the simple logic and sequencing of the system; this is done by a programmable controller, which is more appropriate for this operation.

The programmable controller allows actual interface with the hardware on the production equipment; that is, it will control the opening and closing of valves, switches, and pumps on

the ingredient feed system. The programmable controller receives commands from the computer based on information reported back to it from the production equipment hardware. The programmable controller equipment is programmed using standard relay ladder logic. Most electricians and maintenance personnel are familiar with this type of electrical control representation.

The design and functioning of the ingredient feed and batching system must comply with a number of specifics. It follows that a consistent product from batch to batch results from an ingredient feed system that will deliver all ingredients within very close weight tolerances. Today, flour handling systems are available that will deliver 1000 kg/h of flour, with a tolerance of less than 0.5 kg.

However, there are systems in existence that do not have this same level of accuracy. So quality control, or rather, consistent repeatability of flour weights, can be a problem. These weight variances are reflected in varying moisture content from batch to batch and in the ultimate product quality and consistency.

To compensate for such variances, the system is programmed to calculate the percent variance from the intended delivered weight of flour, and then to deliver the other ingredients in the same proportion. For example, if 1000 kg of flour are required in the flour hopper above the mixer and 100 kg of each of the other ingredients, but if only 950 kg of flour are delivered, then only 95 kg of each of the other ingredients will be delivered. The result is a batch that is only 95% of the intended weight, but the integrity of the recipe and the final product quality is maintained.

This proportional batching is made possible by the computer receiving information from the flour system and then relaying new instructions, via the programmable controller, to the other ingredient delivery equipment. The computer can then accurately record ingredient usage, maintain inventory most accurately and if necessary, call for a larger batch in the next cycle.

Ideally, all ingredients which can be fed in liquid form or which can be prebatched with other liquids are pumped to a set tank mounted on load cells. This set tank can be floor mounted or mounted above the mixer. In the case of a floor-mounted unit, it may receive ingredients from other tanks via a pump or an ingredient premixer. Each separate ingredient is loaded into the tank sequentially, and the weight of each is checked and recorded in the computer. The total mixture is then pumped to the mixer at the appropriate time. When the set tank is mounted above the mixer, the same sequential loading by weight occurs, and gravity feed to the mixer takes place at the appropriate times. There is also provision for the addition of minor ingredients, that is, those that are not bulk ingredients. There are ingredient systems available that include intermediate storage bins from which minor ingredients are automatically fed to the mixer. These subsystems can be used to eliminate manual preweighing of small amounts of ingredients.

Sometimes the sequence of loading each of the ingredients must be varied to suit the particular product. The time phasing (if necessary) of ingredient loading into the mixer can also be programmed into the mixer cycle.

As the purpose of the ingredient feed system and the mixing system is to provide dough to continuous make-up equipment, it is vital that the downstream equipment is neither starved nor choked. To maintain continuous batch harmony and balance, low-level and high-level

detectors are provided in the hoppers of the make-up equipment. These level detectors notify the programmable controller and in turn the mixer when the make-up equipment is ready to receive another batch. In the event of a downstream interruption in the production, the mixer should not discharge until dough is needed. Under normal conditions, when there are no stoppages downstream, the flow of dough to the make-up equipment is controlled by what is called a "cycle delay" timer. The purpose of the cycle delay timer is to synchronize the mixer with the make-up equipment in terms of dough put through per hour.

Normally a continuous mixer does not have an operator, and therefore it is necessary to visually display the various steps in the mixing cycle and to indicate exactly what part of the cycle is being performed. This is done by means of a monitor panel with indicating lights, which shows that the flour valve is open or closed, the mixer is running at slow or high speed, the make-up equipment is either empty or ready for refilling, and the mixer is holding, waiting for the hopper to become sufficiently empty to allow refilling.

These indicating lights are normally green, and are all of the push-to-test type to prevent misinformation, which could occur in the event of a light bulb failure. Below the green lights are a group of red lights, mostly related to safety devices that when tripped will prevent the mixer from functioning. These red monitor lights also indicate any failure of fuses, breakers, starters, or motors, and low air pressure. As with the other monitor lights, these too, are push-to-test type.

The monitor panel does not control anything, contrary to what most people seem to think. It merely displays the various steps in the cycle as they occur. It also indicates tripped safeties or failed electrical components. Then why have it? Because if something goes wrong with an unattended mixer, rapid diagnosis of the problem or unusual situation is essential.

The major benefits and savings resulting from the automation of the batch mixing process are summarized here.

- *Labour savings*: there may be a feeling of skepticism when we say that a mixer can run with no operator. However, on specific lines such as lines for hamburger buns or baguettes, it's perfectly feasible to have no mixing operator.

- *Reasonable cost*: the incremental cost of an automated mixer versus the standard batch mixer is less than the cost of one operator for one shift for one year. This is for the mixer only, and excludes the ingredient feed system.

- *Inventory control*: a computer-controlled ingredient system keeps the most accurate usage records, even when batch sizes vary. The re-ordering of ingredients can be automated. Inventories can be reduced due to the full knowledge of usage and the time phase of that usage. The chances of running out of an ingredient are minimized.

- *Product consistency*: proportional batching ensures consistent recipe balance, regardless of batch size. The ingredient system requires proof that all ingredients are fed to the mixer, thus preventing the omission of an ingredient. The human element is removed.

- *Simplified troubleshooting*: the visually indicated monitors have some diagnostic capability in that they instantly point out anomalies such as tripped safeties, and failures of components which are likely to fail such as fuses, breakers, and possible starters.

Temperature control

During the mixing process, the temperature of the dough rises due to heat generated by the frictional forces and the heat of hydration of the flour. The frictional heat is the result of the mechanical energy one has to put into the dough to overcome internal and external (dough in contact with the side of the mixer bowl) friction that is caused by the dough mixing process. The amount of friction to be overcome is related to water absorption and to gluten development. When the mixing time changes, the friction factor also changes.

The heat of hydration is the energy that is liberated when a substance absorbs water. The amount of heat liberated varies with the degree to which water is absorbed. For soluble substances, energy will be needed to dissolve them, so the change in energy level is negative, as are the amounts of heat withdrawn from the system.

The temperature of the dough is also influenced by other factors such as: temperature of ingredients, size and type of mixing equipment (artofex mixer compared with a high-speed mixer, for instance), batch size (batches that are too small in mixers that are too big), mixing procedures (time, speed), and room temperature.

To cool down the dough and to remove the excess heat generated during the mixing process, the baker can use one of the following methods: add ice to the dough, use chilled water to make the dough, refrigerate the mixing bowl (mainly done in horizontal mixers), use a saturated salt solution which can be cooled down to below 0 °C instead of granulated salt, cool down the ingredients (mainly flour, which can be easily cooled down with the injection of liquid CO_2 during the pneumatic transport).

Calculation of the friction factor

Each mixer is different and each mixer will heat up a given recipe to a greater or lesser degree. The friction factor is defined as the value used to compensate for the temperature increase of the dough during mixing. The friction factor has to be determined experimentally, that is, dough is made with ingredients of which the temperature is known. After the mixing process the temperature of the dough is noted. The friction factor is then calculated as shown in Equation 17.1:

$$3 \times t°C_{dough} - (t°C_{room} + t°C_{flour} + t°C_{water}) \tag{17.1}$$
$$= \text{friction factor}$$

Imagine the temperature of the dough after mixing was 26 °C, the room temperature 23 °C, flour temperature 33 °C, and the water temperature was 12 °C. Then the friction factor shown in Equation 17.2 equals:

$$3 \times 26°C - (23°C + 33°C + 12°C) = 81°C - 68°C \tag{17.2}$$
$$= 10°C$$

Calculation of the desired water temperature

Now, once the friction factor has been determined, it is easy to calculate the temperature of the water needed to obtain a predetermined dough temperature. To make dough of 25 °C in a bakery where the temperature is 24 °C with flour which has a temperature of 30 °C, water of the following temperature will be needed ([Equation 17.3](#)):

$$(3 \times 25°C) - 30°C - 24°C - 10°C = 75°C - 64°C \tag{17.3}$$
$$= 11°C$$

The general formula is shown in [Equation 17.4](#):

$$3 \times t°C_{dough} - (t°C_{room} + t°C_{flour} + friction\ factor) \tag{17.4}$$
$$= t°C_{water}$$

Calculation of the quantity of ice needed

Imagine you need to make dough of 24 °C with flour of 35 °C in a bakery where the temperature is 28 °C. What would the temperature of the water be? The calculation is shown in [Equation 17.5](#).

$$(3 \times 24°C) - (35°C + 28°C + 10°C) = 72°C - 73°C \tag{17.5}$$
$$= -1°C$$

Water of −1 °C doesn't come through the water mains, because ice is a solid. To transform water into ice requires an input of extra energy (latent heat). The change from liquid state to solid state requires quite some energy. This negative energy is liberated when the ice goes from the solid state to the liquid state, and this latent heat is used to cool down the dough. So the question becomes, how much water must be replaced by how much ice? Note that 1 kg of ice = 1 kg of water. To calculate this, one has to use the following formula ([Equation 17.6](#)):

$$[kg\ of\ H_2O(t°C\ water - calculated\ water \tag{17.6}$$
$$temperature)]/(t°C\ water + 80)$$

Example

You have to make dough that contains 100 kg of flour, 62 kg of water, 2 kg of yeast, and 1.8 kg of salt. The temperature of the bakery is 28 °C, the temperature of the flour is 35 °C, and the temperature of the available water is 6 °C. The desired dough temperature is 25 °C. The friction factor for that particular mixer equals 18 °C. How much ice would be needed to achieve this temperature?

First calculate the desired water temperature:

$$(3 \times 25°C) - (28°C - 35°C - 18°C) = 75°C - 81°C$$
$$= -6°C$$

The quantity of ice needed equals:

$$62 \, \text{kg} \times [6°\text{C} - (-6°\text{C})]/(6°\text{C} + 80°\text{C}) = 8.65 \, \text{kg}$$

You will need 53.3 kg of water and 8.7 kg of ice. The ice should be flaked ice to increase the contact surface and to facilitate the liberation of the latent heat.

Degassing the dough

The art of degassing and texturizing doughs is not new to the baking industry. The kneading and degassing of dough has been an important part of the bread making process. The actual means used to degas dough have varied over the years from knocking gas out by hand to mechanical "chewing up" the dough and breaking up the large gas bubbles, causing an even distribution of gas, or expelling the gas. The same can be said of the texturizing process, which has varied from the gentle hand kneading of the bakers' efforts to mechanically texturizing doughs for better overall quality in the final product.

There are several reasons for degassing the dough. The first and perhaps most important reason is the improved scaling accuracy achieved. The savings that can be realized by more accurate scaling of the dough pieces can play an important role when it comes to justifying the capital outlay for a new piece of equipment. Savings in dough piece weight of a couple of grams per piece can result in thousands of euros saved over the long-term life of a degassing machine.

How the weight varies when there is a small interruption of the dough making process is shown in Figure 17.1 and Figure 17.2. A standard deviation in the weight of 2.64 is shown in Figure 17.1. Samples taken immediately after a stop show a standard deviation 2.70; that is, it is not the stop by itself that will introduce more weight variation.
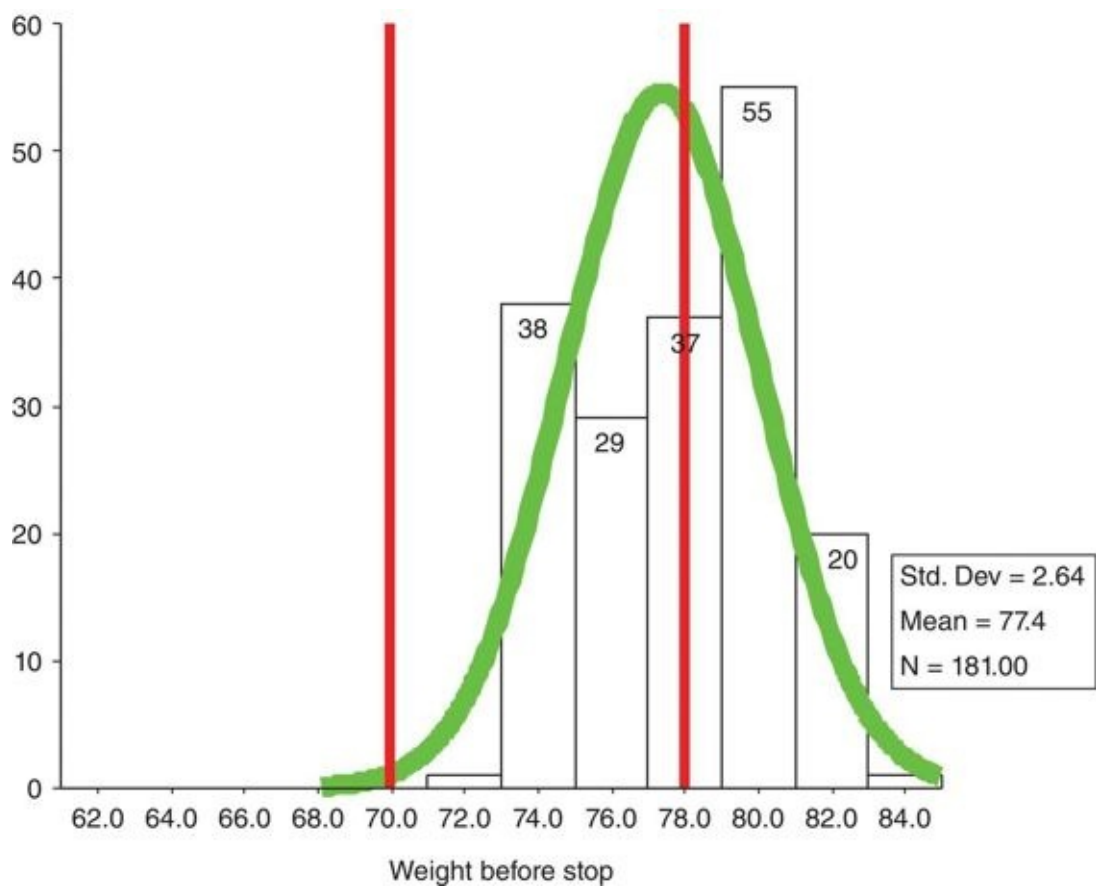
Figure 17.1 Dough weight before stopping bread making process.
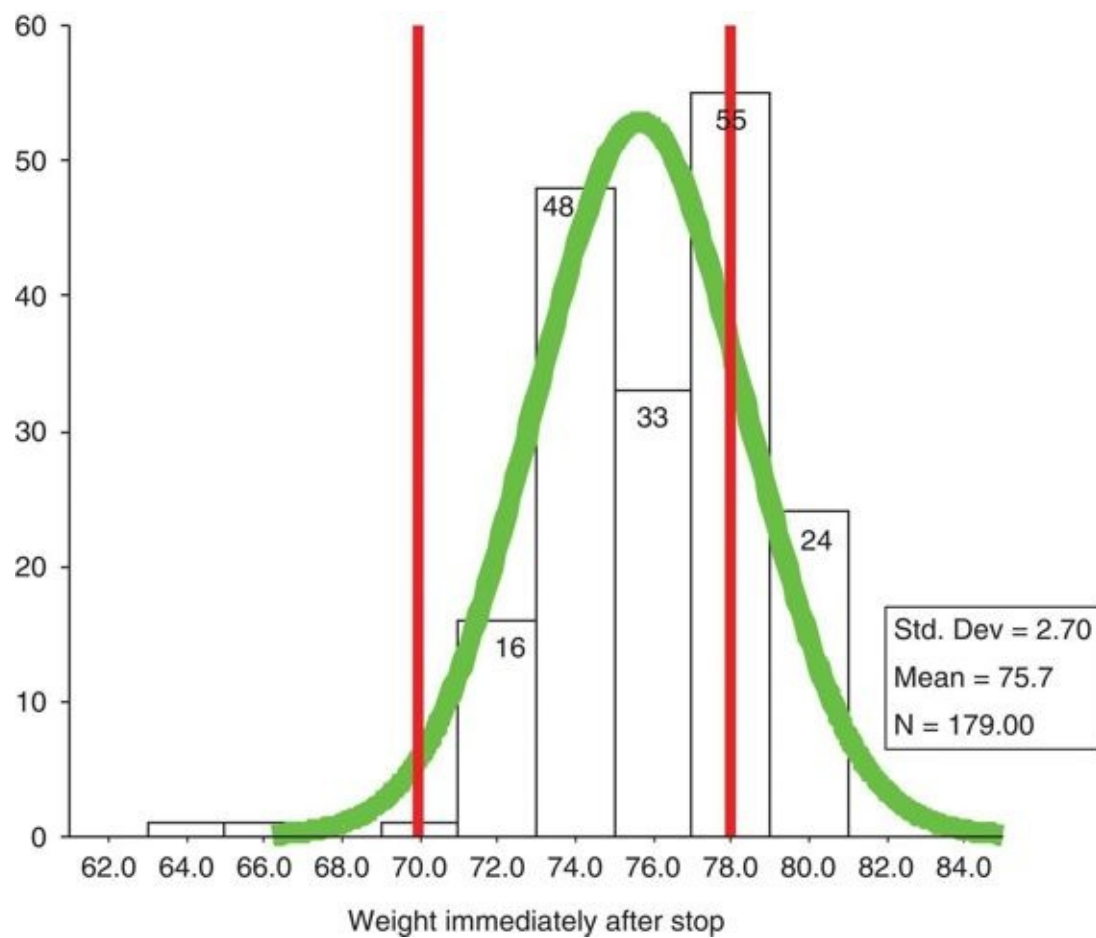
Figure 17.2 Dough weight immediately after stopping bread making process.

The variation in weight after a 10-min stop, however, is shown in Figure 17.3. After 5 min, that the line was running again, the standard deviation of the weight was 2.99; that is, 99.5% of all dough pieces will have a weight that varies between 68.2 and 83.6 g.
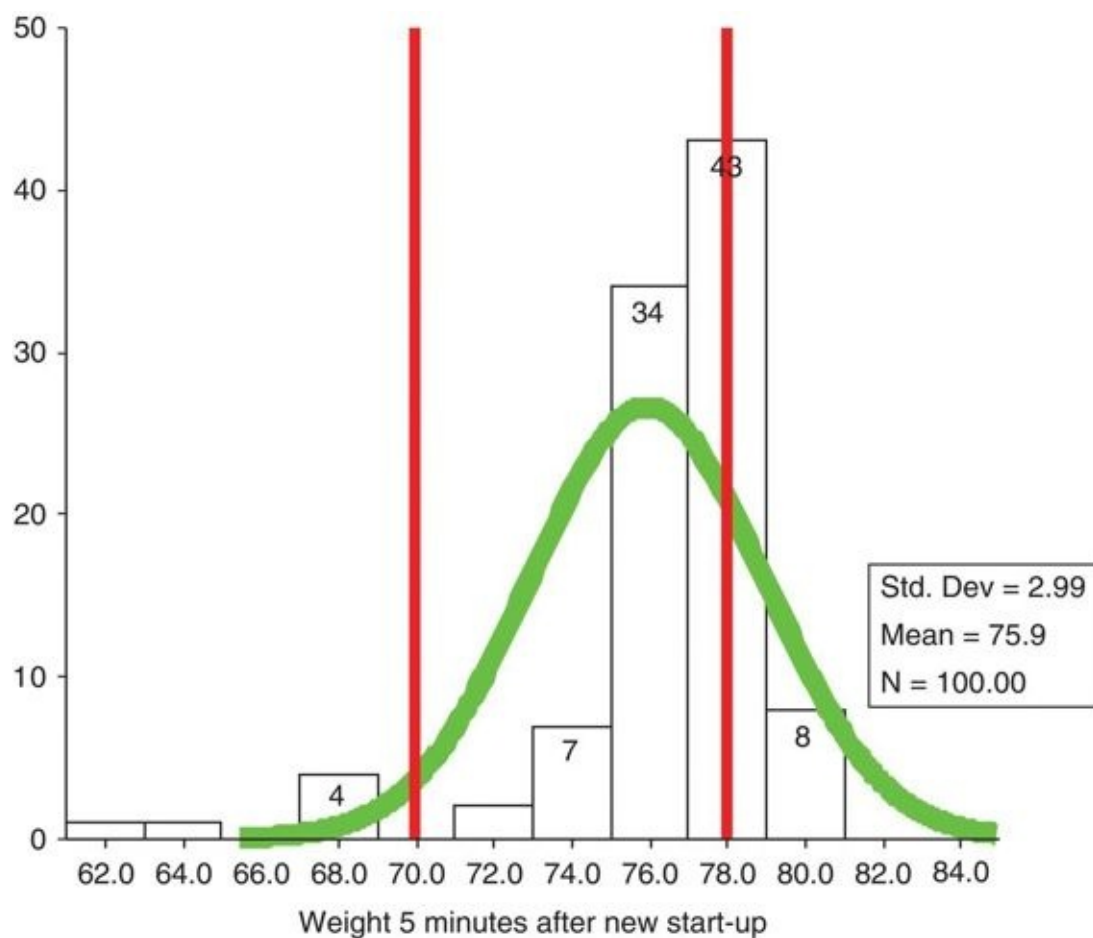
Figure 17.3 Dough weight 5 min after new start-up.

Another reason for degassing the dough would be to increase the run time for a given batch. By degassing the product, larger doughs can be run, since the scaling inaccuracies are minimized from the beginning to the end of the dough.

With the advantage of running larger doughs, there is the additional advantage of being able to minimize the problems caused by short production interruptions. Where previously a short break would have caused scaling problems for the remainder of the dough, degassing the product just before the scaling function allows the dough to be processed with only minor problems.

From the standpoint of quality, a degasser improves the final product by providing a more uniform dough with which to work. This uniformity translates into improved make-up as well as better panning and more even proofing. Basically, the final product has greater uniformity, which means that it is easier to handle during the packaging operation. Fewer problems in packaging mean fewer rejects.

Texturizing the dough

What exactly does "texturizing the dough" mean? In the baking business it means "the developing of the dough cells to form a uniform product structure." There is, of course, more involved than just the cell structure when it comes to texturizing, since strength, color, softness, and cell distribution are all related to the "texture" of the finished product. To the average baker, since the term "texturizing" means more than just cell structure, the reasons for texturizing the dough are diverse.

Texturizing the dough can have a number of distinct advantages including production of uniform density, final mixing and developing, better grain structure, and improved product make-up (Scanlon and Zghal 2001).

Since many texturizing machines are fed by some type of degasser or pump (of either an auger or a lobe type), the texturizing action covers up a multitude of problems created by the degassing/pumping functions. In some applications, the dough is pumped through a pipe and is damaged in the process of getting to the texturizer. The texturizer then acts as an incorporator or mixer and redevelops and disperses the dough so that there are no large pockets of damaged dough in the final product. Also, pipes tend to create larger gas bubbles and non-uniform density in the pumped dough. Texturizers will disperse the gas bubbles and present a dough of a consistently uniform density to the scaling part of the dough processing machine.

Obviously, the two processes of degassing and texturizing cannot be completely separated; they are actually overlapping processes. In dough degassing some texturizing is accomplished, and in dough texturizing some degassing is obtained.

The major advantages of the two processes can be summarized simply by saying that dough improvements in the area of scaling can be realized by degassing, while texturizing the dough gives a better grain structure and improves the overall quality of the final product.

Dough make-up

Once the dough is mixed, it has to be transferred to different parts of the equipment. There are many methods used to transfer doughs from one point to another. The dough may be cut in large pieces by hand and transferred from the dough trough to the mixing machine or to the divider. By locating the mixer on the second floor, the dough can be dumped from the dough trough through a hole in the floor into the divider hopper.

Dough trough hoists have been designed to lift dough troughs filled with fermented sponges to be returned to the mixer to be mixed into doughs. They are also designed to lift remixed doughs to be dumped into the divider hopper.

Other methods available are conveyor systems, dough pumps, and rotary dough feeders. Some doughs – such as doughs for frozen dough products, many different types of speciality bread doughs, and stiff doughs – are not suitable for transfer by a dough pump, one reason being that a lot of heat is created during the transfer process.

Make-up consists of several steps, including dividing, rounding, intermediate proofing, molding, and panning. Major improvements have been made recently in the make-up equipment due to the development of dough conditioners, oxidation agents, and enzymes. The baker is able to produce more pliable doughs by fully developing them in the mixer.

Dough dividers have been developed that punish the dough a great deal less than those used in the past. Dividing and scaling consists of cutting the dough (by hand or mechanically) into loaf size pieces and weighing the pieces to ensure uniformity. Because of the average loss of about 12% during make-up, proofing, baking, and cooling, this loss must be taken into account. One needs 915 g dough to produce a loaf of bread weighing about 800 g. It is of the utmost importance, to ensure a smooth baking process and an even bake, that all pieces weigh approximately the same and that all pieces have the same shape. As baking time is predominately dependent on shape and not on temperature, as most people believe, it is important to remember this during the make-up operations. Dough dividers have a capacity range up to 5000 pieces an hour with a weight varying between 40 and 1200 g.

A divider has a stainless steel conical hopper all the way down to the dough knife, which ensures correct feeding of the dough into the suction chamber. On average, hoppers have a capacity of 100 l (approx. 70 kg of dough).

The dividing mechanism is manufactured from high quality Ni-resistant steel, a dough knife of stainless steel, a suction brass piston, and a measuring piston of food-approved plastic material. This ensures high weighing accuracy and easy handling and cleaning. Dough weight is easily adjustable via a hand wheel. The dough knife has a built in, self-restoring safety release mechanism, protecting the transmission if any hard object should accidentally fall into the hopper.

A specially designed scraper system ensures that the ejected dough pieces drop into the correct position on the discharge conveyor. The two conveyors transport the dough-pieces to the check weigher and rounder. The conveyors are driven by a separate worm gear box which is coordinated with the speed of the machine. It is also possible to fine-tune the adjustment of the speed on the belts. The second belt normally has a higher speed to separate the dough pieces. In most cases a flour duster is mounted, as an option, on the first conveyor. However,

it is important to use as little dusting flour as possible as this flour will not hydrate during the baking process and can be the cause of certain faults in the crumb structure as well as the reason for a dry crumb.

Usually a rounding operation is carried out after scaling. Rounding is the process of making the scaled pieces of dough into round balls with smooth unbroken skin over their entire surface. The unbroken skin will retain the gas generated within the dough piece during the intermediate proofing period, which can be achieved on a conical rounder or a belt rounder. Belt rounders are capable of rounding and sealing the dough without the use of dusting flour. Belt rounders are widely used in rye bread production because the typical conical rounders used for wheat bread are not suitable for rye flour doughs.

Intermediate proofing is the process of giving the rounded dough pieces a short rest period (about 12–15 min) to recover from the effects of the dividing and rounding machine. The rest period allows the dough to relax after undergoing a great deal of mechanical stress from being extruded under high pressure from the divider pockets. Without the rest period the dough would be tight and rubbery and would not go through the molder sheeting rollers without tearing. The intermediate proofing machine has small pockets or baskets covered with canvas travelling within an enclosed temperature- and humidity-controlled area. The most significant new development is the reduction of proofing time in intermediate proofing to 3 min or less due to the development of new ingredients. In spite of this new development, it is the author's personal opinion that there is nothing better than a 12–15 min resting period in a temperature- and humidity-controlled proofing cabinet.

Upon completion of the intermediate proofing period, the dough pieces are molded into the desired shape. In the molder, the dough passes through three distinct stages. Flattening is done in the head rollers of the molder. Second, the sheeting rollers sheet the dough into a flat piece of dough and the curling rollers and thread rollers twirl each piece of sheeted dough and give it a cylindrical shape. Next, the drum or pressure plate rolls and seals the loaf into its final form.

Conventional molders curl the dough in the same direction that it was sheeted. It is difficult to produce bread with a close uniform grain with this type of molder. For this reason, some bakers twist two pieces of dough together or use cross grain molders. Cross grain moulders curl the dough in the opposite direction from which it was sheeted. That is, the dough is caused to turn right or left after it has been sheeted and is then curled. This is called cross grain molding. Cross grain molding and twisting two pieces of dough together prior to putting them into the baking pan produce loaves with a close, smooth grain and texture.

Pan proofing is the process of rolling the panned and racked molded dough pieces quickly into the dough proofing cabinet, which is well insulated and maintained at a temperature of 95–98 °F and a relative humidity of 85%.

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18
Fermentation

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Introduction

Around 3000 BC, fermented bakery products were first developed by ancient Egyptians. The major microorganisms involved in fermentation are yeast and lactic acid bacteria. In Europe, lactic acid fermented dough (sourdough) has been a part of diets for 5000 years. Sourdough has also been traditionally used as a leavening agent in various wheat and rye flour based products for a long time (Ganzle and others 2008). The variation in fermented bakery products depends on the flour variety, ingredients, and fermentation technology used. In 19th century, however, industrial scale baking was developed, and the most common leavening agent was changed to baker's yeast – *Saccharomyces cerevisiae* (Corsetti and Settanni 2007). The dough making process may have one or two fermentation stages (also known as proofing). To reduce quality variation and cost in industrial production, however, the straight dough process has always been used.

Currently, there is a major worldwide interest in healthier products, so there has been renewed significant interest in sourdough bakery products, which have health benefits and unique flavors (Ganzle and others 2008). This has encouraged researchers to try to understand more deeply the mechanisms of fermentation and their impact on the quality of these fermented bakery products. This chapter discusses the fermentative microorganisms, the fermentation mechanisms and their impacts on product quality, and how to monitor change during fermentation.

Microorganisms and fermentation in bakery products

Baker's yeast fermentation

In the late 19th century, commercial yeast for dough making was introduced. Yeast was grown in aseptic systems to ensure only suitable strains could be selected. Today, baker's yeast is regarded as *Saccharomyces cerevisiae*. Media for the inocula should be composed of sugars, minerals, vitamins and salts, and the number of yeast cells can be effectively increased with intensive aeration. In addition, the nutrient feed, pH regulation, and temperature monitoring should be carefully controlled. Bakers' yeast is produced in both wet and dry forms. The wet form (also known as cream yeast) contains around 82% moisture. Shelf-life at 2–4.5 °C is around 3–4 weeks. In contrast, the dry form can be kept for a longer period at ambient temperature. A tunnel or conveyor belt dryer is used to remove moisture. The dry yeast is subsequently rehydrated before the dough making process. The lag phase can be extended until the yeast adjusts to the new environment. To eliminate this step of rehydration, a fluidized-bed dryer is recommended to increase particle porosity, resulting in so-called instant dry yeast. Therefore, the instant dry yeast can be mixed directly with other ingredients. In addition, some antioxidant agents may be added, and of course the packaging may be designed to further reduce the effect of oxygen. This type of yeast is called protected active dry yeast (Kulp 2003).

Lactic acid bacteria fermentation

Lactic acid bacteria used in traditional sourdough are employed variously to develop a diversity of flavor and texture in bakery products. Generally, these bacteria can be classified into three groups including obligate homofermentative bacteria (such as *Lactobacillus amylovorus, La. acidophilus, La. farciminis, La. mindensis, La. crispatus, La. johnsonii, and La. amylolyticus*); obligately heterofermentative bacteria (such as *La. acidifarinae, La. brevis, La. fermentum, La. reuteri, La. rossiae, La. frumenti, and La. zymae*); and facultative heterofermentive bacteria (such as *La. plantarum, La. pentosus, La. casei, La. paralimentarius, and La. alimentarius*).

Robert and others (2009) reported that the dominant *Lactobacillus* species in sourdoughs from wheat flour were *La. plantarum, La. curvatus, La. paracasei, La. sanfranciscensis, La. pentosus, La. paraplantarum, La. sakei*, and *La. brevis*. In rye flour sourdoughs, *La. reuteri* was found to be the dominant and stable microorganism, possibly due to production of the antibiotic reutericyclin. *Enterococcus, Lactococcus, Leuconostoc, Pediococcus, Streptococcus*, and *Weissella* species are less frequently used (De Vuyst and others 2009). In Amaranth flour sourdoughs, *La. sakei, La. plantarum* and *Pediococcus pentosaceus* were reported as the dominant microorganisms (Sterr and others 2009). Competitiveness of microorganisms in sourdough mainly depends on the type of substrate, fermentation temperature, acidity, and interaction among the microorganisms (De Vuyst and others 2009).

Lactic acid fermentation starts with glucose. By using homofermentative lactic acid bacteria, glucose is converted into lactic acid through glycolysis, resulting in two molecules of adenosine triphosphate (ATP). Hexose fermentation through glycolysis can be also conducted by facultative heterofermentative lactic acid bacteria, because they contain fructose-1,6-

diphosphate aldolase, which is a key enzyme for glycolysis. In heterofermentation, not only is lactic acid produced, but also carbon dioxide gas, acetic acid, and ethanol through the 6-phosphogluconate/phosphoketolase (6-PG/PK) pathway. Redox potential of the fermentation system regulates the ratio of acetic acid to ethanol, and this pathway yields one molecule of ATP.

Nonetheless, two molecules of ATP are possibly obtained when fermentation starts at pentose. The obligate heterofermentative lactic acid bacteria should be used because they contain phosphoketolase, which is a key enzyme in the 6-PG/PK pathway. Pentose is phosphorylated and converted to ribulose-5-phosphate or xylulose-5-phosphate which enters the lower half of 6-PG/PK pathway. Pentose phosphate is then cleaved into two compounds – glyceraldehyde-3-phosphate (GAP) and acetyl phosphate – to produce lactic acid and ethanol, respectively. Two molecules of ATP can be obtained by phosphorylation of GAP. In facultative heterofermentation, phosphoketolase can react with pentose and, therefore, facultative heterofermentative lactic acid bacteria can ferment pentose in the same way as the obligate heterofermentative lactic acid bacteria. Pentose fermentation results in the equal production of lactic acid and acetic acid without formation of carbon dioxide gas (Corsetti and Settanni 2007).

Sourdough

Sourdough is a mixture of flour (usually wheat flour or rye flour) and water, fermented with lactic acid bacteria with or without the addition of yeast. Depending on the preparation process and the metabolic activity of the main lactic acid bacteria, sourdough can be classified into three types (Decock and Cappelle, 2005) as shown in Table 18.1.

Table 18.1 Classification of sourdough

Sourdough	Description	Microorganisms
Type I sourdough	A mixture of flour and water that is incubated at low temperature (< 30 °C) with a continuous back-slopping by using the mother sponge taken from the previous fermentation, in order to keep the metabolic activity of microorganisms at high rate.	*La. brevis, La. plantarum, La. paralimentarius, La. rossiae La. sanfranciscensis*
Type II sourdough	A mixture of flour and water that is incubated at high temperature (> 30 °C) for long fermentation time (up to 5 days) with addition of leavening agent. This sourdough can be liquid and is widely used as an acidifying agent and an aroma carrier.	Heat and acid tolerant microorganisms such as: *La. amylovorus, La. fermentum, La. pontis, La. reuteri.* Leavening agent: *Saccharomyces cerevisiae*
Type III sourdough	A dried sourdough which includes lactic acid bacteria and leavening agent. Microorganisms in an active state are first transformed to a latent state by drying and then reactivated later. The number of the revitalized microorganisms is dependent on the drying conditions. A dried sourdough can be used as a starter in premixes.	Heat tolerant microorganisms Leavening agent: *Saccharomyces cerevisiae*

To make bakery products using type III sourdough, dried sourdough is mixed with flour and other dry ingredients prior to dough making. The typically recommended ratio of dried sourdough to flour is 1 : 9. Firstly, dough is kept at approximately 40 °C for revitalization of the selected microorganisms. During this period, other contaminating microorganisms can also be revitalized, resulting in a reduction of the selected microorganisms and spoilage of the dough culture. After revitalization, the temperature should be reduced to approximately 30 °C for normal fermentation of the selected microorganisms.

Interaction between yeast and lactic acid bacteria in sourdough

In the fermentation system that includes yeast and lactic acid bacteria, the maximum growth rate of yeast is reduced due to the presence of the lactic acid bacteria. Ethanol production by yeast is also therefore decreased; however, the final cell counts of yeast are not affected. On the other hand, yeast fermentation enhances the production of mannitol and acetic acid by the lactic acid bacteria (Paramithiotis and others 2006). Stability of the lactic acid bacteria population can be determined by the rate and intensity of acidification. Normally, stability of the lactic acid bacteria should be observed every few days (De Vuyst and others 2009). However, acidification may vary depending on environmental parameters including temperature, time, and water content. For example, incubation at 25 °C for 4 h slightly decreases pH, compared to incubation of the same duration at 37 °C (Gaggiano and others 2007). To ensure a high degree of acidification and flavor development, microorganisms

should be selected from their transition and stationary phases for sourdough making.

Saccharomyces cerevisiae is one of the most frequently found yeasts in the sourdough fermentation, and this may be because baker's yeast is used so commonly in bakeries that it can effectively become a contaminant. In the presence of lactose and whey protein in dough, however, Cabellero and others (1995) reported superior proofing activity of *Kluyveromyces marxianus* compared to *Saccharomyces cerevisiae. Kazachstania exigua* and *Candida humilis* are other yeasts frequently found in sourdough. Due to their maltose-negative and acid-tolerant characterization, *Kazachstania exigua* and *Candida humilis* should be fermented together with maltose-positive lactic acid bacteria such as *La. sanfranciscensis*. During fermentation, *La. sanfranciscensis* hydrolyses maltose through the activity of an intracellular maltose phosphorylase without ATP utilization, resulting in unphosphorylated glucose plus glucose-1-phosphate. The unphosphorylated glucose is then excreted outside the cells and used by the maltose-negative yeasts, that is, *Kazachstania exigua* and *Candida humilis*. Without the maltose-negative yeasts, the unphosphorylated glucose may be excreted; as a result, glucose repression is induced in maltose-positive yeasts (De Vuyst and others 2009). Therefore, interaction between yeasts and lactic acid bacteria significantly affects the stability of the sourdough fermentation.

Mechanisms during fermentation

Generation of carbon dioxide gas

Carbon dioxide gas is generated during yeast fermentation, according to Equation 18.1. The generation rate is related to the number of yeast cells and rate of metabolism of yeast.

$$C_6H_{12}O_6 + yeast \rightarrow 2CH_3CH_2OH + 2CO_2 + yeast \qquad (18.1)$$

After carbon dioxide gas is generated, it migrates towards the initial nuclei of air bubbles (which are formed during mixing), to develop a foam-like structure with pores. As a result, dough volume is expanded. The curve of dough volume expansion during the period of proofing can be characterized in three phases including lag, growth, and stationary phases. The lag phase is the time taken for the initial yeast fermentation and for the carbon dioxide gas produced to diffuse towards the air nuclei. The subsequent phase is where the dough expands to reach the maximum volume. In the last phase, the gas generation rate is balanced by the rate of gas leaving the dough. Therefore, the volume expansion remains constant. The optimum proofing time can be defined as the time required for dough expansion to reach the maximum possible volume. Dough growth in terms of the volume expansion ratio ($y(t)$) can be simulated by the modified Gompertz equation (Equation 18.2) (Romano and others 2007):

$$y(t) = \alpha \exp\left(-\exp\left(\frac{\mu e}{\alpha}(t_{lag} - t) + 1\right)\right) \qquad (18.2)$$

where α is the maximum relative volume expansion ratio, μ is the maximum specific volume growth rate, t_{tag} is time during lag phase and e is the Neper number.

In addition, dough volume expansion is also accelerated by increasing proofing temperature because a higher temperature speeds up yeast activity and decreases gas solubility (Chiotellis and Campbell 2003). Relative humidity during proofing is another parameter affecting dough properties and thereby gas retention (Therdthai and others 2007). The number of pores and the dough volume can be analyzed using the magnetic resonance microscopy technique. During proofing, the number of pores in dough is dramatically increased and is described by the Boltzmann sigmoidal function (Equation 18.3):

$$YF(t) = \frac{A}{1 + \exp(-(t - t_0)/\Delta)} + B \qquad (18.3)$$

where A is amplitude, B is offset, t_0 is time lag and Δ is the transition interval.

Development of exopolysaccharide

During lactic acid fermentation, exopolysaccharide is possibly developed, resulting in the change of viscoelastic properties of dough and thereby bread itself. Exopolysaccharides

include homopolysaccharides (containing one type of monosaccharide, either glucose or fructose) and heteropolysaccharides (containing a combination of monosaccharides such as glucose, galactose, and rhamnose) (Bounaix and others 2010). Exopolysaccharides (such as glucans, fructans, glucooligosaccharides, and fructooligosaccharides) have been claimed as a gut health promoter (Poutanen and others 2009). *Lactobacillus sanfranciscensis* could produce fructans that stimulate bifidobacterial growth, thus acting as a prebiotic. These substances developed during fermentation were recognized as safe, resistant to high acidity, and resistant to high temperature during baking (Corsetti and Settanni 2007).

With the addition of sucrose (glycosyl donor), homopolysaccharides can be synthesized by extracellular glucans and glycosyltransferase. Heteropolysaccharides are synthesized intracellularly from sugar nucleotides by glycosyltransferase. In addition to synthesis of exopolysaccharides, acid is formed and may affect both the volume and taste of bakery products (Corsetti and Settanni 2007). The development of heteropolysaccharides reduces resistance to deformation and elasticity of sorghum sourdough. As a result, specific volume of bread can be increased, whilst hardness of bread crumb can be decreased. However, the effect of the heteropolysaccharides on the viscoelastic properties of wheat sourdough is not significant due to the strong gluten network in wheat dough (Galle and others 2011).

Proteolysis

During wheat dough fermentation, major proteins including glutenins (both high molecular weight (HMW) and low molecular weight (LMW)) and gliadins are degraded through proteolysis. This involves proteolytic enzymes including the proteinase group and peptidase group. The proteinase can firstly catalyze protein degradation to produce a small fraction of peptides; the peptides are then hydrolyzed and broken down by peptidase, resulting in amino acids. Fermentation of wheat germ by *La. plantarum* LB1 and *La. rossiae* LB5 could increase the concentration of free amino acids by 50%, particularly leucine, lysine, phenylalanine, valine, histidine, alanine and methionine. *In vitro* protein digestibility was also significantly increased ($p \leq 0.05$) (Rizzello and others 2010). The hydrolysis of peptides is enhanced by acidic conditions, and so the production of lactic acid through lactic acid fermentation, which can reduce pH to around 3.5−4.0, can result in optimum conditions for the activity of proteinase. However, these conditions would not enhance the degradation of HMW proteins. In addition to acidification, *La. pontis* can reduce disulfide bonds in gluten proteins. As a result, the solubility of dough proteins can be increased and become more accessible to the activity of enzymes (Ganzle and others 2008).

The HMW glutenins are responsible for dough strength and elasticity, while the LMW glutenins are responsible for dough viscous properties. The dough viscous properties are also affected by gliadins which are monomeric alcohol soluble proteins. Therefore, the degradation of glutenins and gliadins causes modification of the viscoelastic properties of dough. In bread, the extent of proteolysis should be limited, although some proteolysis is desirable for the production of amino acids, which may be converted by browning reactions to flavor molecules during baking. In contrast, extensive protein degradation might be required in some products such as soda crackers. Moreover, proteolysis has been recommended as an alternative process for the production of bakery products for persons with celiac disease (Poutanen and others 2009). Generally, proteolysis is controlled by enzyme reactions and by the solubility of glutens. To increase the amount of proteolysis, a combined technique can be

used involving the addition of protease, chemical acidification to optimize the pH for enzymatic reaction, and the addition of a reducing agent to reduce intermolecular and intramolecular disulfide bonds, thereby increasing the solubility of proteins and their accessibility to enzymes.

Synthesis of volatile compounds

The concentration of volatile compounds in dough is very low, but it plays an important role in sensory quality and particularly regarding a fresh taste. Major volatile compounds strongly influencing the bakery flavor include organic acids, alcohols, esters, aldehydes, and carbonyls. They can be synthesized during both fermentation and baking. Baking generates crust flavors through Maillard reactions and caramelization depending on the degree of baking and related process conditions. The resulting flavor comprises roasty, malty, and sweet notes. Poinot and others (2008) reported that a decrease in yeast content may affect the quantity of the flavor, because yeast contributes to the formation of Maillard reaction precursors.

Fermentation is mainly responsible for crumb flavor depending on the types of microorganisms used, the material substrates, and fermentation conditions. Proteolysis during lactic acid fermentation yields amino acids which are converted to aldehydes and alcohols via the Ehrlich pathway (Corsetti and Settanni 2007). Poinot and others (2008) reported that volatile compounds in fermented bread included ethyl acetate, ethanol, 2,3-butanedione, 1-propanal, 2-methyl-1-propanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 3-hydroxy-2-butanone, acetic acid, propionic acid, benzaldehyde, isobutyric acid, butyric acid, isovaleric acid, hexanoic acid, and phenylethyl alcohol. Rizzello and others (2010) reported alkanes and alkenes as major volatile compounds arising from the fermentation of wheat germ by *La. plantarum* LB1 and *La. rossiae* LB5.

Homofermentative lactic acid bacteria tend to produce a high amount of aldehyde groups. Flavor compounds such as ethyl acetate and hexyl acetate are generated from the fermentation of heterofermentative lactic acid bacteria. As heterofermentative lactic acid bacteria produce both lactic acid and acetic acid, the ratio of lactic acid to acetic acid is another important factor affecting aromatic profiles in heterofermentation. To obtain enough volatile compounds, lactic acid fermentation requires 12–24 h. However, flavor generation time can be shortened to a few hours in the presence of yeast fermentation.

When yeast fermentation is used alone, flavor generation time is longer, compared to a combination of yeast and lactic acid fermentation. The intensity of flavor compounds can be increased by adding some sugars. Torner and others (1992) observed the high intensity of flavor compounds from yeast fermentation in dough when either glucose or sucrose was added. However, addition of maltose did not show significant flavor improvement. During storage, the volatile compounds in yeast leavening products reduce quickly, whereas in general the flavor of bakery products can be maintained for a longer period with the addition of sourdough. Moreover, addition of kefir into the sourdough bread can slow the rate of decrease of the concentration of total volatile compounds during a 5-day storage. As a result, freshness of the bread was maintained for longer, compared to bread without kefir (Plessas and others 2011).

Change in starch digestibility and availability of minerals and vitamins

Changes in pH can selectively enhance the performance of some enzymes. In turn, the activity of enzymes and microbial metabolites affects the nutritional availability of, for example, starch, vitamins, and minerals (Poutanen and others 2009). Due to acidification from sourdough fermentation, it was observed that pH was decreased and starch digestibility was retarded. Moreover, the level of soluble carbohydrates (glucose, fructose, sucrose, maltose, and raffinose) were decreased (Rizzello and others 2010). A decrease in pH to 4.1–4.5 could also slow down digestion rate. Acetic acid and propionic acid formed during heterofermentation could prolong gastric emptying rate. Therefore the glycemic index may be decreased (Poutanen and others 2009). This is due to the effect of the lactic acid fermentation, rather than the activity of yeast.

In the presence of phytate (myo-inositol hexaphosphate), the bioavailability of minerals may be limited. Therefore, phytase should be added to increase the bioavailability of minerals. Flour contains some phytase, but the level might not be sufficient to reduce the amount of phytate (Corsetti and Settanni 2007). Yeast and lactic acid bacteria also contain phytases, which can dephosphorylate phytate and form free inorganic phosphate and inositol phosphate esters which have less influence on mineral solubility and bioavailability than phytate. It was found that the reduction of pH to 5.5 through sourdough fermentation, resulted in the amount of phytate being decreased by 70% (Poutanen and others 2009).

Cereal products are a good source of vitamins such as folate, thiamine, and vitamin E; for example, 45–70% of the folate in bread is from yeast (Patring and others 2009). During yeast fermentation, the folate content in both wheat and rye dough can be increased three-fold in the best case. Similarly, thiamine and riboflavin content could be increased during a long period of yeast fermentation. The increase in folate, thiamine, and riboflavin in dough is also mainly from yeast fermentation, rather than lactic acid fermentation. In addition, no synergistic effect from the yeast and lactic acid bacteria on the contents of vitamin B group was observed. During sourdough fermentation, some losses of vitamin E were observed (Poutanen and others 2009).

Synthesis of antifungal compounds

Bakery products, particularly yeast leavening products, are often spoiled by fungi such as *Aspergillus, Cladosporium, Endomyces, Fusarium, Monilia, Mucor, Penicillium*, and *Rhizopus*. Such spoilage can be prevented naturally by sourdough addition. During heterofermentative fermentation, acetic acid and lactic acid are produced and these act as antifungal compounds. The fungistatic effect of acetic acid is more significant than that of lactic acid. Among the heterofermentative lactic acid bacteria, *La. sanfranciscensis* was claimed to have the most effective antifungal activity due to the production of a mixture of acetic, caproic, formic, propionic, butyric, and *n*-valeric acids. *La. plantarum*, one of the most widely used strains in sourdough, also provided long-term effective antifungal activity even after baking, due to the production of phenyl-lactic acid and 4-hydroxy-phenyl-lactic acid (Corsetti and Settanni 2007).

Fermented dough making processes and monitoring systems

In dough fermentation, either a natural fermentation or a starter induced fermentation can be used. The use of natural fermentation may result in variation of the quality of the fermented dough due to variable types and amounts of microorganisms in the system. Fermentation using a starter proceeds with higher numbers of microorganisms and less variation of microbial counts; it is easier to control the fermentation and hence the consistency of the fermentation process. Therefore, industrial bakers prefer fermentations using starters.

Straight dough processes

The straight dough process is simple and quick. All ingredients are mixed in a single stage and allowed to bulk ferment for 3–4 h, therefore quality of the fermented dough may be quite variable. To improve dough quality, knocking-back (punching down the dough) can be integrated into the original fermentation process, to partially degas the dough and to redistribute the yeast and substrates after an initial fermentation for 1–2.5 h. Therefore, gas production rate is kept high and dough volume is improved and controlled. Moreover, salt and fat may be added at the knocking-back step, instead of making the additions at the beginning with the other ingredients. The delay of salt addition can allow a rapid dough development at the beginning, while the delay of fat addition can make dough more tolerant to mechanical forces (Kulp 2003).

'No-time' dough process

The 'no-time' dough process involves a very short fermentation time which is achieved by increasing the number of fermentative microorganisms. In the straight dough process, the required level of compressed baker's yeast should be around 2.5%. However, with the 'no-time' dough process, the level of baker's yeast should be increased to 3.5%. This reduces fermentation time at 30–35 °C and 85% relative humidity by 2 h. The quality of the dough developed through using the 'no-time' process may be poorer than that developed by the straight dough process, due to insufficient fermentation time. Therefore, some reducing agents such as l-cysteine (40 ppm) may be added to enhance gluten maturity (Kulp 2003).

Sponge and dough process

Unlike the straight dough process, ingredients for the sponge and dough process are divided into two lots. The first lot, including flour (around 50–80% of total), yeast, and other ingredients are mixed with water, to obtain fairly stiff dough called '*sponge*'. The sponge is fermented for 3–5 h to develop a web-like structure which enables gas retention. After 60–70% of the fermentation time, the dough may collapse. Then the second lot of ingredients is mixed with the sponge using high-speed mixing, and this mix is allowed to ferment for another 15–30 min to complete the required volume expansion. The sponge and dough process is widely used in bread making in the United States. In the United Kingdom, fermentation time for the development of sponge is very long (about 12 h) because only one-

third of total flour is used. To speed up this UK approach, a greater quantity of yeast is used, and this modification is called '*flying sponges*' (Kulp 2003).

Monitoring systems during fermentation

As dough evolution is one of the most important steps affecting the final quality of bakery products, various methods have been developed for monitoring dough expansion during fermentation (Table 18.2). The monitoring system should be non-destructive and enable on-line measurement, in order not to interfere with dough evolution. Measurement level may vary from macroscopic to microscopic structures. Recently, image analysis has been developed to monitor macroscopic structures such as dynamic dough density and shape ratio. Porosity can be monitored by video image analysis and X-ray tomography. The distribution of pores, which are the microscopic structures, can be monitored by magnetic resonance imaging. In addition, the detection of variation in ultrasonic velocity can be used to monitor the kinetics of dough fermentation.

Table 18.2 Monitoring system for dough expansion during fermentation

Measurement	Method	Reference
Dynamic dough density	Digital image analysis	Soleimani Pour-Damanab and others (2011)
Macroscopic structure: porosity and shape ratio of dough	Video image analysis	Shehzad and others (2010)
Microscopic structure: pore distribution	Magnetic resonance imaging (MRI)	Bajd and Serša (2011)
3D cellular structure and porosity evolution	X-ray tomography (XRT)	Babin and others (2006)
Kinetics of dough fermentation by monitoring the change in ultrasonic velocity	Acoustic waves using low frequency ultrasound	Skaf and others (2009)

Conclusion

Fermentation is one of the most important steps in bakery product production after mixing. It is mainly related to yeast (particularly baker's yeast, *Saccharomyces cerevisiae*) and lactic acid bacteria (heterofermentative microorganisms are preferred). The metabolic activities of fermentative microorganisms are responsible for the quality of dough and hence the quality of the final bakery products. Yeast fermentation with sugar as the substrate generates carbon dioxide gas which later migrates toward the centre of bubble nuclei, resulting in an increase in dough volume during fermentation. Fermentation with heterofermentative lactic acid bacteria yields lactic acid (which decreases pH), acetic acid (which acts as an antifungal agent), exopolysaccharides (which can act as a gut health promoter), and volatile compounds (which act as a flavoring agent). In addition, protein is degraded during fermentation through proteolysis to yield amino acids, which promote yeast growth and enable the development of Maillard flavor compounds. Therefore the fermentation process affects the structure, texture, flavor, and shelf-life of bakery products. To control the consistency of fermentation, starters (such as baker's yeast, type II sourdough in liquid form, and type III sourdough in dry form) are preferred in industrial scale baking rather than relying on natural fermentation. The types of fermentation process include the straight dough process, and the sponge and dough process. To monitor the parameters of dough expansion during fermentation, non-destructive measurement using video image analysis, MRI, XRT, and acoustic waves has been developed.

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19
Baking

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Introduction

During baking, heat and mass transfer takes place in the dough simultaneously and interdependently, and involves four major changes:

1. Gases are vaporized as temperature increases; the gas cell increases in volume provided that the cell wall retains gases and is deformable.

2. Starch gelatinizes upon the increase of temperature to an extent depending on the local availability of water, and proteins coagulate. These changes limit dough extensibility. It may limit the cell expansion described in (1), and hence be a local driving force for pressure build-up and possibly fracturing of the cell wall (3).

3. The initial structure with closed gas cells separated by dough walls is transformed into a porous structure with interconnected pores, known as the dough-crumb transition. Dough membranes rupture when they can no longer withstand the gas pressure, and changes in (2) are a possible cause. In theory, ruptured walls limit the cell expansion described in (1); gas molecules are exchanged between adjacent open cells, and finally transported out of the dough. Pressure forces in such regions may then decrease, a possible explanation for the collapse of cells locally.

4. Under the action of high temperatures at boundaries, water vaporizes in the oven atmosphere. Depending on the product thickness, but also on baking conditions, this supports the formation of a dry, hard crust in dessert or bread dough, and may also lead to a complete drying in biscuits and cookies. This is accompanied by specific chemical reactions (in particular Maillard reactions), responsible for the browning of the crust and the development of flavour. Early setting of the crust restricts total volume and modifies the balance in pressure forces between the inner and outer dough and hence cell expansion (1) locally.

Oven-rise (the change of dough dimensions during baking, look at a video at http://www.weekendbakery.com/posts/baking-bread-the-movie/) together with dough/crumb transition and crispiness are the most outstanding macroscopic features of baking, with relevance to texture. Reactions are another essential feature, related to taste (production of flavour), digestibility (starch gelatinization), and safety (production of acrylamides).

These different changes do not occur sequentially but do overlap. Roughly in the first stage of baking, cell expansion and water loss begin; one of these can, however, be delayed during this stage. During stage 2, both the total height of the product and the rate of water loss reach their maximum. Color develops at the surface during the last stage 3, concomitantly to a possible collapse of the porous structure and a decrease in the rate of water loss. These changes are detailed in the following sections.

Heat and water transport during baking

Temperature dominates product quality because it affects enzymatic reaction, volume expansion, starch gelatinization, protein denaturation, non-enzymatic browning reactions, and water migration, as will be detailed later.

Time-course changes in temperature and its distribution through the dough during baking are determined by multiple factors, among them: the size of the product (biscuit versus bread loaf); the ratio between top, side and bottom heat flows; the expansion of cells which reduces thermal conductivity, but likewise favors the transport of water vapor evaporated at the surface layers to the core, where it condenses and releases energy.

Modes of heat transfer

Heat is transferred through the combination of conduction, convection and radiation. Radiation comes from the heating elements (burner flames) and all hot metal parts (walls) in the oven. It is responsive to changes in the absorptive capacity of the dough and there is a tendency for color changes upon heating to accelerate after the first browning has occurred (Therdthai and Zhou 2003). Contribution of radiation to heat transfer at the top surface can be estimated by h-monitor and was found to be much higher in direct ovens, 70–80% (Baik and others 1999, 2000a) than in indirect ovens, 45–60% (Fahloul and others 1995). The contributions of the different heat sources were calculated through modeling for tunnel type multizone industrial ovens; for biscuit, heat transferred by conduction through the band was minimal (10%), radiant and convective heat being of the same order (Fahloul and others 1995). Conduction represents more than half of the total heat transferred to the product during tin baking, possibly reaching two-thirds in certain conditions (Baik and others 2000a). Conduction mode is also predominant for products deposited on the hearth of the oven, like Indian flat bread (chapatti) (Gupta 2001) or some French breads (Sommier and others 2005).

Modes of heat transport into the dough

As soon as the product is introduced in the oven, heat transfer results in superficial water evaporation and heating up of the product. In the oven, where the temperature is high, the partial water vapor pressure is far from saturation. Hence, water vapor in the superficial layers of the product diffuses into the oven atmosphere. As the diffusive flow of liquid water from the core is less than the flow of evaporated water at the surface, the product dries at the surface, leading to a very low water activity, and the water activity decreases rapidly with water contents below 0.15 kg/kg. Temperature near the product surface does not exhibit a marked plateau at 100 °C (the temperature of water at the pressure close to that of the atmosphere, and water activity close to that of pure water). Above 100 °C, the temperature rises in thermodynamic equilibrium with the locally decreasing water content and rises towards that of the oven temperature.

Under the dough surface, where there is still liquid water, water evaporates to saturate the partial water vapor pressure in the pores. The water vapor pressure reaches a maximum at a location from which the vapor can diffuse in two directions, towards the dough surface and towards the core. The driving force for the transport of water vapor from this location to the

surface has been detailed earlier. On the other hand, the temperature gradient induces a water vapor pressure gradient between this location and the core, which produces a diffusive flow of vapor in the same direction. Because the water migrates counter to the thermal gradient, it is accompanied by condensation, release of its latent heat and an increase in liquid water at the core. This is why this mechanism is also called transport by "evaporation-condensation". This mechanism takes place as long as a temperature gradient remains (and water remains!) and the core temperature has not reached 100 °C. Such transport is promoted by the opening of the porous structure which occurs during baking; nevertheless it also proceeds in a cellular structure (closed cells) with four distinct phases (De Vries and others 1989):

1. evaporation proceeds on the warmer side of the gas cell,

2. water migrates through the gas phase, induced by the vapor concentration gradient inside the cell,

3. water condenses on the colder side of the gas cell,

4. liquid water is transported by diffusion through the dough wall to the warmer side of the next gas cell, where the series of processes starts again. Thorvaldsson and Skjöldebrand (1998) suggested, however, that as the condensed water is likely to be absorbed by starch gelatinization, transport of water by this mechanism to and through the ungelatinized closed region is unlikely to occur.

The transfer of water vapor with vaporization near the surface and condensation at the core contributes to heat transfer, and was proposed by Sluimer (cited by De Vries and others 1989) to explain rapid heat transport during baking. De Vries and others (1989) recorded the temperature in the centre of gas-free and fermented doughs during baking with the same external dimensions, and showed that heat transport in fermented dough was much faster than in gas-free dough. If conduction was the only mechanism, heat transport in a gas-free dough should have been faster than in fermented dough pieces because of cells acting as isolating elements. Such results were explained by the contribution of the evaporation-condensation-diffusion mechanism to heat transport.

The location where the partial water vapor pressure is at maximum progressively moves inside the product, making the dry area grow thicker. Progressively, the superficial dry layer constitutes a major barrier to heat transport inside the product, hence temperature and water content gradients at the core progressively vanish. Heat transport is no longer intensified by the diffusion of water vapor to the core. In high-moisture products, temperature at the core stabilizes at 100 °C; this plateau lasts as long as its water content remains similar to that of the dough.

Measurement of temperature during baking

Reproducible measurements of the temperature inside dough during baking are difficult owing to the oven-rise and to the difficulty of accurately locating the thermocouples. Temperature gradients are considerably increased in thin dough pieces (about 15–50 °C in 2 mm thick biscuits), amplifying the inaccuracy in positioning the thermocouple. Thermal conduction along the thermocouple wire is an additional source of bias; however, this can be overcome by using optic fibers of less accuracy. Nevertheless, some general trends can be

drawn for the core.

Heating rate in bread is close to 3–6 °C/min in the absence of steam injection (Therdthai and Zhou 2003; Sommier and others 2005; Patel and others 2005; Wagner and others 2007). Patel and others (2005) reported higher heating rates at the core for small bread loaves, of 15–17 °C/min. Higher heating rates can also be generated by steam condensation onto the dough/batter surface subsequently to its injection into the oven. Sommier and others (2005) and Chevallier and others (2002) reported heating rates of 25 °C/min for bread (baguette) and 37–150 °C/min for short dough. In a tunnel type multizone industrial oven, heating rates in the range of 18–50 °C/min were reported for cakes (Baik and others 2000a).

Spatial distribution of water in bakery products

Whatever the type of bakery product it is important to realize that moisture gradients exist in the product at the end of the baking process. Such distribution in water content through the product governs textural properties such as the contrast between the softness of crumb and the crispiness of the crust in high-moisture bakery products. It governs more generally the storage properties of the product such as the loss in crispiness in high-moisture products or the checking of biscuits (Ahmad and others 2001; Saleem and others 2003). Heat transport towards the centre during baking induces water transport and therefore a change in the water distribution (refer to the heat transport subsections). Water also plays an important role in the major structural changes that take place during bread baking, at the microscopic (for example, water vaporization in the cell expansion) and molecular scale (for example, starch gelatinization).

The initial water content typically ranges from 11 to 30% for biscuit and crackers (Wade 1988), 32–38% for cake batter (Baik and others 2000b) and 38–48% for bread dough.

The final moisture of a freshly baked biscuit is usually within the range of 1–5% depending on the type of product (Wade 1988). Water distribution is very difficult to measure in the thickness of a biscuit; it can be however assessed by simulation or experimentally along the diameter of a disk-shaped biscuit, with differences up to 1.7% (Ahmad and others 2001). The final water content in cakes varies between 17 and 24% (Baik and others 2000b).

As bread loaves are larger pieces, reports of final water content are scarce for the loaf as a whole, with most data concerning the distribution of moisture through the loaf. Total water loss can be between 10 and 20%; it is enhanced by higher baking temperatures (Hasatani and others 1992). The lowest water content at the end of baking is obviously encountered in the bread crust, being 2–15% depending on the permeability of crust (Hirte and others 2010) or the oven temperature (Ahrne and others 2007). Bread crumb located beneath the crust exhibits intermediate water contents, from 2– to 12% lower than that of dough (Thorvaldsson and Skjöldebrand 1998) or from 3–9% lower than that of dough (Wagner and others 2007). The crumb at the core retained its initial moisture content or even increased (Wagner and others 2007). When sampling took place just after removal of bread loaves from the oven, an increase in water content by 1 to 3% was reported at the core (De Vries and others 1989; Zanoni and Peri 1993; Wagner and others 2007). In addition to the conventional, destructive method of sampling combined with oven-drying for water content determination, a continuous method based on near infrared reflectance (NIR) was proposed by Thorvaldsson &and Skjöldebrand (1998). Light was sent into the sample through an optic fibre and the

intensity of the reflected light was measured. The technique is known to be sensitive to the structure and temperature of the sample. If dependence on temperature was incorporated into the calibration, structural dependence made quantitative measurements in the sample difficult during the oven-rise. Thorvaldsson &and Skjöldebrand (1998) showed an increase in water content in the core immediately after the local temperature had reached $70 \pm 5\,°C\,°C$ (i.e. after cell expansion was more or less complete), which reached +8% at the end of baking (35 min at 225 °C °C) relative to that of dough initially.

Magnitudes of the overall drying rate were 1.8×10^{-3} kg kg water/kg dry matter for cookies (Hayakawa and Hwang 1981), 1.4×10^{-3} to 9.4×10^{-4} kg kg/kg for yellow and chocolate cakes of various sizes (Baik and others 2000b), 2.5×10^{-4} kg kg/kg for sponge cake (Lostie and others 2002) and 2.8×10^{-5} to 2.4×10^{-4} kg kg/kg (Hasatani and others 1992) and $2-5 \times 10^{-4}$ kg kg/kg (Sommier and others 2005) for bread.

Measurements of water content in bakery products

In practical terms, although the overall water loss is easy to assess, the determination of water content profiles in crumb during baking requires the setting up of a method for accurate cutting of the loaf into samples while still hot and deformable, and the minimization of water losses by evaporation from cut surfaces. Water content is also sensitive to the time elapsed from the end of baking and the relative humidity in the atmosphere of storage; these important factors are rarely reported and make experimental results almost impossible to compare between studies.

Cell expansion and squeezing, crumb formation, and overall collapse

During baking, total volume may increase by 16–100% (volume unit per 100 volume units of the initial dough) for bread (Zanoni and Peri 1993; Sommier and others 2005; Wagner and others 2008), 50–80% for sponge cake (Lostie and others 2002) and 100–300% for biscuit (Wade 1988; Chevallier and others 2002).

Growth from gas nuclei

The presence of gas nuclei is a prerequisite for inflation (Baker and Mize 1937). The aeration of dough or batter is achieved during mixing or whipping for sponge cake. For bread, dough porosity after mixing is in the range 3–15% depending on the mixer type and mixer speed (Cauvain and others 1999). The inflation of cells may be started before baking by fermentation, while sheeting – involved in the production of cream crackers for instance – largely eliminates the gas produced from previous steps of processing within the dough (Wade 1988).

Mechanisms favoring volume increase in cell

Thermal expansion of gases initially occluded in the bubble is responsible for 10–15% of cell inflation. Further inflation is hence supported by the vaporization of dough components at the cell–dough interface; vaporization is hastened by temperature increase during baking. The solubility of carbon dioxide accumulated during fermentation decreases during baking and the dissolved gases are vaporized. The vapor pressure of water increases rapidly upon heating; the same applies to ethanol accumulated during fermentation, although this gas has received little attention in past studies. It is important to understand that water vapor is the predominant gas for cell inflation in specific bakery products like sponge cake (Lostie and others 2002) or non-yeasted puff pastries. Finally, most biscuits, cookies, and cakes are chemically aerated, the most commonly used reagents being sodium bicarbonate, alone or with an acidulant, and ammonium bicarbonate. With sodium bicarbonate, for instance, the hydrogen ion reacts with the bicarbonate ion to produce water and carbon dioxide, the latter supporting cell inflation. The decrease in H^+ concentration is accompanied by an increase in pH in the batter. This is slightly counterbalanced at the end of baking by the decrease in overall water content (Baik and others 2000b).

Mechanisms limiting volume increase in cell

Mechanisms resisting or limiting the expansion are multiscale, from molecular scale (for example, stiffening subsequent to starch gelatinization), microscopic scale (for example, ruptures in cell walls and opening of the porous structure) to macroscopic scale (for example, pores connected to the exterior of the dough or setting of the outer layers of dough). Few studies have encompassed all these different scales in attempting to provide a clear explanation for controversial data and theories in the literature. In this context, the relative contribution of the different mechanisms to the restrictions of expansion will not be

discussed further as more multiscale research is required.

Starch gelatinization

Starch gelatinization and/or protein aggregation contribute to the stiffening of dough (Figure 19.1) and reduce the capacity of cell walls to elongate and the gas cell to increase in volume. Some evidence has been obtained when studying the early interruption of the baking process, the most demonstrative case being the growth of columnar cells in crumpets where heat transfers unidirectionally (Pyle 2005). As a consequence, the onset temperature of these reactions (in the vicinity of 60 °C for starch gelatinization and 70 °C for protein aggregation) is often related to a build-up in gas pressure and the restriction of, and ultimately the cessation of, cell growth. This molecular mechanism would favor the influence of gases with low temperatures of vaporization on cell expansion, highlighting a contrasting effect of temperature rise which favors gas production on the one hand but limits dough extension on the other hand. However, pressure measurements recently performed at different locations in bread dough with miniaturized sensors showed no temperature-dependence of the pressure build-up during baking (Grenier and others 2010); this result questions the assumed relationship between dough stiffening and pressure build-up, but could be explained if ruptures in the cell walls occur simultaneously or earlier (see later). In addition, neither of these explanations seems to apply to biscuit or cookie baking. Chevallier and others (2002) observed that the cessation of the oven-rise in biscuit, which occurred in the temperature range of protein aggregation, was usually followed by collapse, hence questioning the rigid character of the dough matrix produced by protein aggregation.
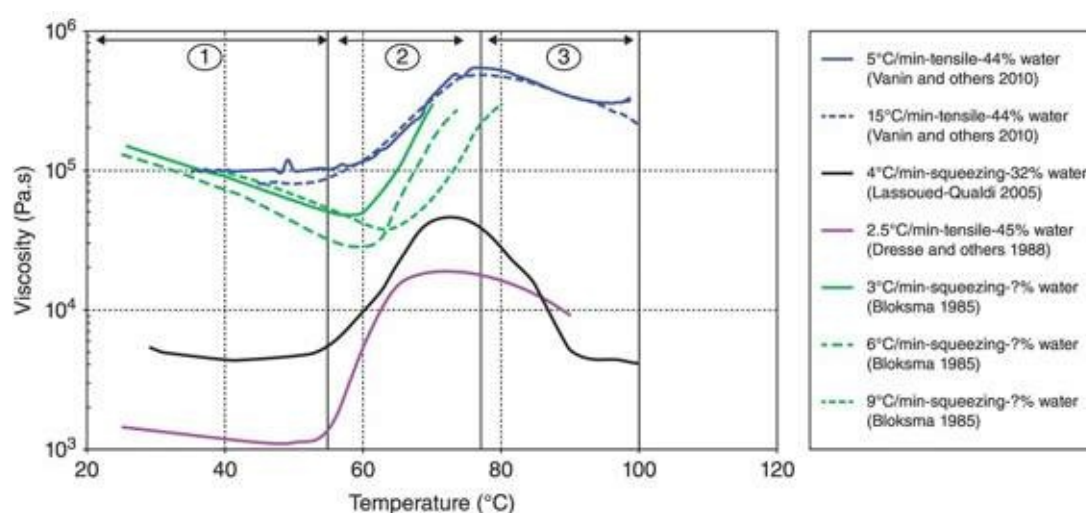
Figure 19.1 Wheat dough viscosity as a function of temperature, a compilation of literature data, where 'squeezing' means the use of the testing mode employing biaxial deformation (lubricated squeezing mode), and 'tensile' means the testing mode employing uniaxial deformation. Refer to the text for more details about stages 1, 2, 3.

Ruptures in cell walls

Ruptures in cell walls and the formation of an open porous structure are evidenced by observation of a product section with the naked eye or with microscopy (Lostie and others 2002), as well as by the uniformity in pressure as reported at the end of baking or during post-chilling (Grenier and others 2010). Nevertheless, closed pores would still remain at the end of baking, occupying a still uncertain volume fraction, of 1–20% (Datta and others 2007). Rupture in cell walls is a prerequisite for limiting cell shrinkage upon cooling and for

preserving the oven-rise. Drastic shrinkage of bread loaves formulated with tapioca starch was related to the absence of ruptures in cell walls (Kusunose and others 1999).

Pressure gradients between neighboring cells tend to promote rupture. In the literature, rupture in cell walls is very often assumed to be due to the pressure build-up subsequent to dough stiffening. Mizukoshi and others (1980) working on biscuit dough heated in a liquid paraffin bath observed the formation of bubbles on the dough surface and the massive emission of gas towards the exterior of the bath as soon as the internal temperature of the sample exceeded that of protein coagulation (70–90 °C in the presence of sugar). For optimal oven-rise, Eliasson and Larsson (1993) also recommended adjusting the thermal gradient inside the bread dough to the strength of the gluten film forming the interface of cells.

Rupture is more generally determined by the extent and rate of deformation in cell walls; resistance to rupture can hence be modulated by dough formulation (high protein content in the flour, low water content in dough, addition of emulsifiers) and/or the mastering of the mixing step in terms of under- or over-kneading (Dobraszczyk and Salmanowicz 2008). Consistently, dynamic monitoring by MRI showed that for low interference of the crust setting, the expansion of bread dough ceased locally at temperatures lower than the onset temperature of starch gelatinization, a result which was associated with early ruptures in cell walls (Wagner and others 2008). In this study, an influx of gas higher than the outflux was supposed to maintain the open porous structure and avoid its collapse until its setting by starch gelatinization.

The net balance between influx and outfluxes is crucial for evaluating the impact of the pore opening on cell expansion: for tin baking, mass exchange between the bottom region and the exterior is limited by the tin walls and also the dough core structure becomes porous later, limiting exchange of the bottom region with the top region and the oven; the bottom is hence likely to retain its gases despite ruptures in cell walls and, as a result, the porosity will expand proportionally more than in other regions, by a factor of two to four (Wagner and others 2008).

Setting of the crust and its effect of cell collapse or coalescence

Early crust setting is an additional, macroscopic determinant of cell expansion. There is minimal interference by the crust with local cell inflation if crust setting occurs (just) after the dough at the core has expanded (Wagner and others 2008) (Figure 19.2a). The reverse is, however, more frequently encountered in realistic baking conditions (Figure 19.2b). The intensity of the crust interference depends on the dynamics of dough stiffening at the product surfaces and heat transport to the dough core, supporting cell inflation.

(a)

Region 4
Region 3
Region 2
Region 1
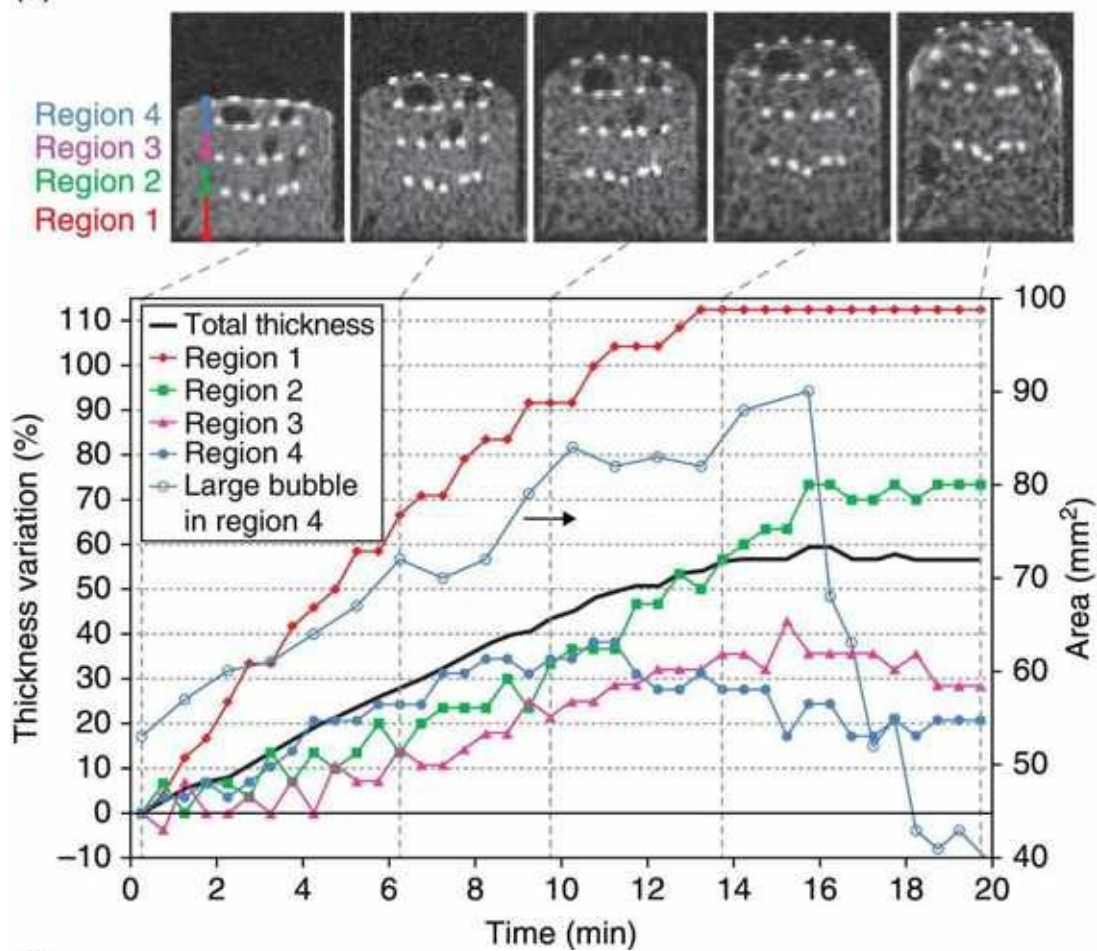
(b)
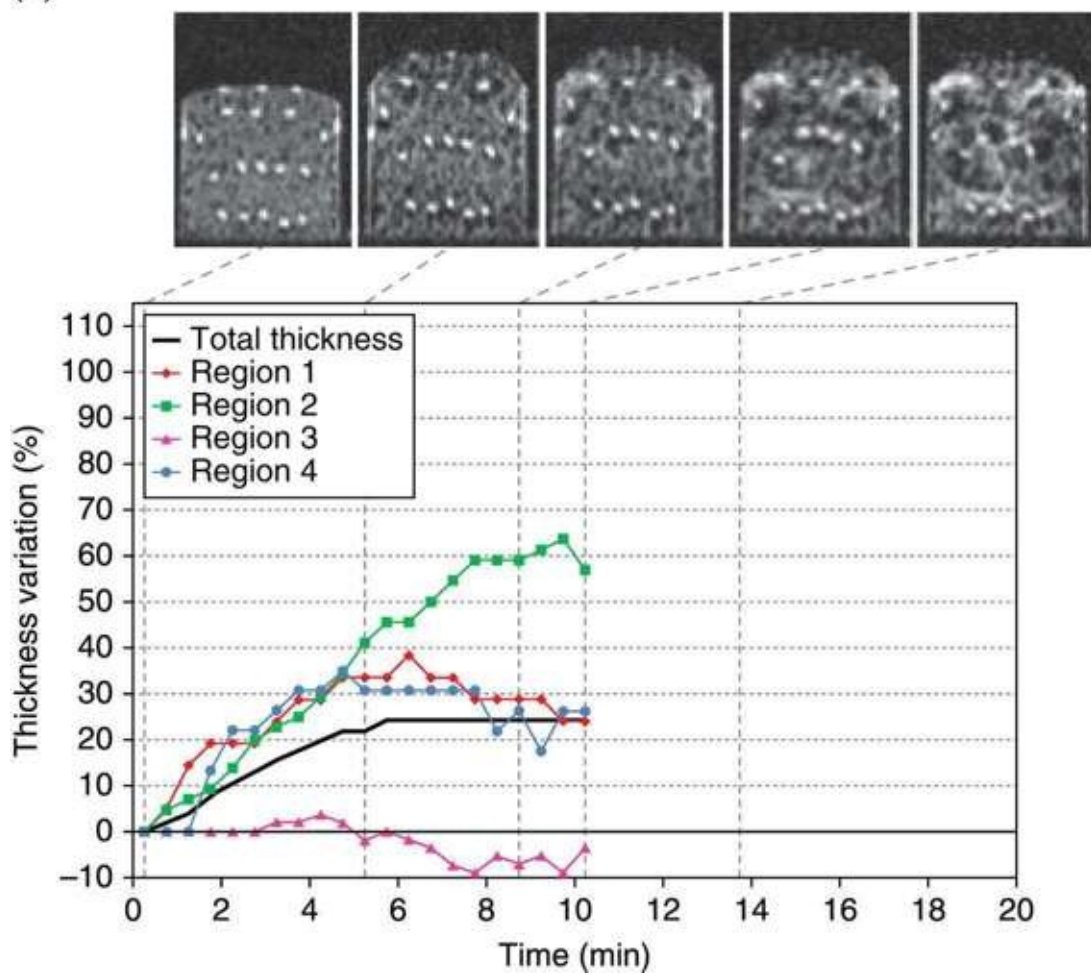
Figure 19.2 Changes in local porosity as monitored by MRI during bread pan-baking (Wagner and others 2008. Reproduced with permission of Elsevier). Dough regions are separated by one or two rows of oil microcapsules of which a high MRI signal (bright spots) permit the tracking of dough displacement subsequent to bubble inflation. Heat is transferred from bottom and top faces only. Associated MRI images are displayed at the top of each sub-Figure 19.for selected baking times; high signal intensity is related either to oil microcapsules (bright spots) or to dense regions of crumb especially present during the second part of baking. The tracking of microcapsules in case b was stopped when crumb structure became too dense in their vicinity (see last image). (a) case of late crust setting (oven temperature 130 °C): the different regions stop expanding all together; final porosity is unevenly distributed because of the limited mass transfer at the bottom (next to the baking tin); standard deviation from three repetitions was less than 3% in thickness variation (b) case of early crust setting (oven temperature 180 °C): inflation at the core (region 2) occurs after the cessation of the overall expansion and proceeds at the expense of the other regions which get squeezed.

Crust setting results in a constant total volume; if the crust sets early, it is accompanied by the building of pressure at the core, resulting from the vaporization of gases under limited increase in cell volume (Grenier and others 2010). The pressure build-up particularly concerns the unbaked region with closed pores. The force exerted by the core on other dough regions becomes higher as baking progresses; thus, the core inflates at the expense of other dough regions in which gas gets compressed, resulting in a reduction in volume as visualized by MRI (see Figure 19.2b), and/or an increase in pressure (Grenier and others 2010). The amount by which a cell collapses is determined by the extent to which the cell wall is set when it ruptures (Jefferson and others 2007). If the cell wall is completely set when it fractures, the outward pushing of the inner part of the dough will have no squeezing effect; if a cell wall is still partly flexible, it will be at least partly squeezed. The relationship between dough stiffening and rupture is hence crucial; the greater the separation between the two events, the less the degree of squeezing (Jefferson and others 2007). Since these events are often associated with threshold values of temperature, and the dough is heated from the outside mainly by conduction, the outer crumb (beneath the crust) is more prone to squeezing. Zhang and others (2007) developed a device with a fabric lid placed above the top surface of a bread pan and which made it possible to stop the oven-rise at different heights. Using MRI they showed that the later the oven-rise was stopped, the deeper the location of the squeezed crumb. Consistently with the above mechanistic sequence, this result was explained by the isotherm of wall rupturing moving deeper into the product as more time was allowed for heat transport into the dough. A wider temperature gradient would be expected to develop in larger cells, which are more prone to squeezing (Jefferson and others 2007). The growth of a large cell followed by its squeezing upon the expansion of the dough core is shown in Figure 19.2a; a cell formed in the bread dough at the end of fermentation might no longer exist in the final baked structure of the loaf. Because of these force balances developing in the dough, changes in local porosity are not monotonic during baking, and phases of compression and inflation occur alternately. Thus, the outer layers of bread may be 2−3 times denser than the initial dough (Jefferson and others 2007).

The increase in pressure generated by the crust setting also imposes additional stress on the cell walls, possibly leading to bubble coalescence in the still unbaked part of the product and finally to coarse texture of the crumb. Hayman and others (1998) mimicked the crust setting

by applying to the top of the bread pan various levels of over-pressure and at different baking times. They found that an over-pressure of 0.3 kPa applied when the temperature at the dough core was between 60 and 70 °C accentuated the coalescence between neighboring cells, as shown by the more open-grain crumb structure of the final bread slices. When pressure was continuously monitored inside bread dough during baking, sudden falls in pressure were associated with bubble coalescence, which was frequently observed at the dough core and less frequently elsewhere (Grenier and others 2010). These pressure drops started at 40 °C and stopped at 70 °C; dough stiffening that proceeds beyond this temperature may render the coalescence more difficult. Pressure drops were also more frequent when higher pressure gradients were developed such as for short-proved doughs (Grenier and others 2010).

The increase in pressure generated by the crust setting may also lead to its own rupture, allowing prolongation of the oven-rise, but also contributing to strong spatial heterogeneity in crumb expansion as monitored by MRI for bread (Wagner and others 2008) or X-rays for cake (Whitworth 2008).

Finally, pressure build-up in bread is accompanied by a release of CO_2 (Zhang and others 2007). The net balance of the two mechanisms on cell expansion has not been assessed to date; despite the release of CO_2, pressure build-up might be favorable to cell expansion. On the other hand, CO_2 release may be desired since it is assumed to be a vector of aroma compounds (Eliasson and Larsson 1993).

Collapse of products

The collapse of products is often reported in the literature, and to significant extents. For example: −13% (Hayman and others 1998) and −30% (Zanoni and Peri 1993) for bread, −20 to −25% for sponge cake (Lostie and others 2002), and −100 to −150% for biscuit (Chevallier and others 2002). Nevertheless, this phenomenon has received little attention so far. Two main hypotheses have been proposed to explain it: (i) the insufficient rigidity of the matrix to overcome the effect of gas loss or increase in permeability (Chevallier and others 2002); (ii) the late shrinkage of the crust subsequent to cross-linking reactions such as extensive protein coagulation and Maillard browning reactions (Sommier and others 2005).

Total water loss

Whatever the type of bakery product, it is important to realize that moisture gradients exist in the product at the end of the baking process. The distribution in water content through the product governs thesection). Water also plays an important role in the major structural changes that take place during bread baking, at the microscopic (e.g. water vaporization in the cell expansion) and molecular scale (for example, starch gelatinization).

Measurements of water content in bakery products

In practical terms, although the overall water loss is easy to assess, the determination of water content profiles in crumb during baking requires a method to be set up for the accurate cutting of loaf samples while still hot and deformable, and the minimization of water losses by evaporation from cut surfaces. Water content is also sensitive to the time elapsed from the end of baking and the relative humidity of the storage atmosphere; these important factors are rarely reported and make experimental results between studies almost impossible to compare.

Spatial distribution of water content in different bakery products

The initial water content typically ranges from 11 to 30% for biscuit and crackers (Wade 1988), 32–38% for cake batter (Baik and others 2000b), and 38–48% for bread dough.

The final moisture of a freshly baked biscuit is usually within the range 1–5%, depending on the type of product (Wade 1988). Water distribution is very difficult to measure in the thickness of a biscuit; it can, however, beBread crumb located beneath the crust exhibits an intermediate water content, reported as being 2–12% lower than that of dough which was at 42% (Thorvaldsson and Skjöldebrand 1998) or 3–9% lower than that of dough which was at 49% (Wagner and others 2007) or at 3% itself (Marston and Wannan 1976). The crumb at the core retained its initial moisture content or it even increased (Wagner and others 2007). When sampling took place just after removal of bread loaves from the oven, an increase in water content by 1–3% was reported at the core (De Vries and others 1989; Zanoni and Peri 1993; Wagner and others 2007). In addition to the conventional, destructive method of sampling combined with oven-drying for water content determination, a continuous method based on near infrared reflectance (NIR) was proposed by Thorvaldsson and Skjöldebrand (1998). Light was sent into the sample through an optic fiberThorvaldsson and Skjöldebrand (1998) showed an increase in water content in the core immediately after the local temperature had reached 70 ± 5 °C (that is, after cell expansion was more or less complete), which reached +8% at the end of baking (35 min at 225 °C) relative to that of dough initially.

Magnitudes of the overall drying rate were 1.8×10^{-3} kg water/kg dry matter for cookies (Hayakawa and Hwang 1981), 1.4×10^{-3} to 9.4×10^{-4} kg/kg for yellow and chocolate cakes of various sizes (Baik and others 2000b), 2.5×10^{-4} kg/kg for sponge cake (Lostie and others 2002), and 2.8×10^{-5} to 2.4×10^{-4} kg/kg (Hasatani and others 1992) and $2-5 \times 10^{-4}$ kg/kg (Sommier and others 2005) for bread.

Structural changes in starch and protein during baking and subsequent changes in dough/crumb mechanical properties

Basic mechanisms of starch gelatinization

Starch gelatinization comprises a series of processes on a molecular scale, which overlap in time: (i) swelling, that is the absorption of water by the starch granules and the increase in volume of these starch granules; (ii) hydration-facilitated melting whereby the crystalline structure of the granules is irreversibly lost, and (iii) disruption of starch granules owing to further hydration of the disordered polymer chains, followed by the partial dispersion of amylose and amylopectin. Amylose association increases as the concentration of soluble amylose increases and when the temperature is less than the melting temperature of amylose crystallites (Morris 1990). Granular swelling together with exudation of amylose from granules, are responsible for the increase in viscosity.

Starch gelatinization is an endothermic process, and the number of endothermic transitions (one to four) depends on dough composition, mainly water content (Figure 19.3). The first and second endothermic transitions reflect the disorganization (melting) of starch crystallites; third and fourth endothermic transitions (endotherms) are attributed to the dissociation of amylose–lipid complexes that formed in the previous process steps. Attainment of the first two endotherms is accompanied by the loss of birefringence, which is characteristic of native starch (Burt and Russell 1983). The extent of starch gelatinization during baking can be estimated by the quantity of heat uptake as assessed during calorimetric analysis relative to a reference; the reaction follows first-order kinetics (Marcotte and others 2004).
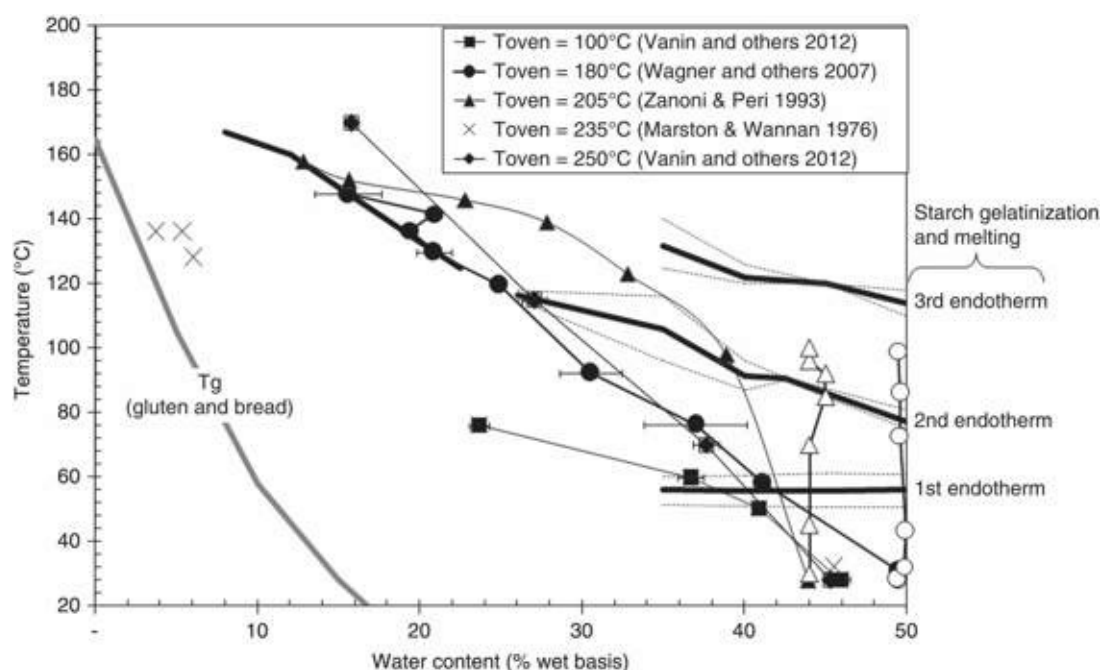
Figure 19.3 Heat-moisture pathways of crust (filled symbols) and crumb (open symbols) from the literature, as represented in the state diagram of starch and gluten, and where T_{oven} is the oven temperature.

Factors affecting starch gelatinization and extent of starch gelatinization in bakery products

In the presence of sodium chloride or sucrose at low concentrations, gelatinization occurs at slightly higher temperatures, and is less complete as evidenced by lower enthalpies of melting (Biliaderis 1991; Ghiasi and others 1983). Marcotte and others (2004) reported a peak gelatinization temperature in the presence of cake ingredients in the range 94–97 °C. Fats and emulsifiers also generally delay gelatinization (Richardson and others 2003). In the temperature range 60–70 °C, a high level of activity of α-amylase in doughs causes enzymatic breakdown of gelatinized starch, which in turn attenuates the increase in viscosity normally associated with gelatinization. As a result of the limiting amount of water and/or the presence of co-solutes, the starch is only partly gelatinized in many baked products. The degree of gelatinization is low in dry products, such as biscuits, where a considerable degree of birefringence can still be observed after baking (Wade 1988). Up to 70% of the starch granules gelatinize at the center of a bread loaf (Biliaderis 1991); some starch granules lose their birefringence but still appear intact, whereas other are disrupted. The partially swollen granules usually become stretched into elongated forms enabling gas cells to expand.

The swelling of starch granules as observed by light microscopy is also affected by the heating rate. A higher heating rate increases the temperature range over which the granules increase in size; it also results in incomplete folding of granules (Patel and Seetharaman 2006). These differences potentially result in altered patterns of amylose leaching, phase separation from amylopectin and network formation, possibly accounting for the differences in gel properties and baked product texture (Patel and others 2005).

Protein coagulation

Heating above 60 °C also gradually modifies the protein network, with the polymerization of glutenins and the changes from gluten gel to coagel. In dough, water does not migrate rapidly; thus, every starch granule gelatinizes by using the water in or near the granule. As there is insufficient water in the dough to gelatinize completely, some of the water will transfer from the protein membranes to the starch as the baking proceeds. This is facilitated by protein denaturation upon heating, a reaction which is accompanied by water release. However, some of the water will remain unavailable for starch gelatinization (Ghiasi and others 1983). Therefore starch gelatinization and protein coagulation both affect the diffusion of water by absorbing and releasing water, respectively.

Impact on dough viscosity during baking

Data for viscosity in dough at constant water content as reported in past studies (Bloksma 1985; Dreese and others 1988; Lassoued-Oualdi 2005; Vanin and others 2010) are compared in Figure 19.1. Note that these studies differed in the heating rates used, and two different testing modes were used: biaxial deformation (lubricated squeezing mode) or uniaxial deformation (tensile mode). Nevertheless, the same amplitude of variations in dough viscosity was observed, with three distinct phases at around the same transition temperatures of 55, 75 and 100 °C.

1. Firstly, the logarithm of viscosity slightly decreased until the dough temperature reached

around 55–60 °C (phase 1, Figure 19.1). Phase 1 was not observed in all studies, especially when the values to be measured were below the sensitivity threshold of the measuring apparatus (Lassoued-Oualdi 2005; Vanin and others 2010). This decrease in viscosity in dough is common to all materials in which no transformation takes place.

2. Between 55 and 75 °C, an almost linear increase in the logarithmic viscosity was observed (phase 2, Figure 19.1). This phase was attributed to the starch gelatinization (in particular the swelling) and/or to protein coagulation; their relative contribution remains unclear (Dreese and others 1988; Lassoued-Oualdi 2005). The temperature at which the viscosity is minimal becomes higher as the dough is heated more rapidly (Bloksma 1985); this is explained by the finite rate of starch structure changes governing the increase in viscosity.

3. Between about 75 and 100 °C, the logarithmic viscosity decreased almost linearly (phase 3, Figure 19.1). This was not observed in all studies, because either the range of temperature was limited in the upper values (Bloksma 1985) or the water content in the sample started to decrease above 95 °C (Vanin and others 2010). Two possible mechanisms governing phase 3 were proposed (Lassoued-Oualdi 2005; Vanin and others 2010): (i) the gas nuclei originally present in the dough, and those formed at the mixing stage, might expand upon heating, or (ii) the gelatinized starch grains become much softer and disrupt; both hypotheses affect measurement and lead to a reduction in the modulus. During the testing of different hydrothermal pathways under rheological measurements, however, the passage of the second endotherm (associated with the melting of the remaining crystallites) was directly linked to the onset of viscosity decrease (Vanin and others 2012), a conclusion which supports the latter hypothesis.

It must be emphasized here that the uniaxial tensile mode gave results in coherence with lubricated squeezing measurements leading to biaxial extension of the dough, as expected around the cell. These tests were performed at high extension rates compared to the ones involved during baking, however, being between 1 and $2 \times 10^{-3}\,\text{s}^{-1}$ (Bloksma 1985), and this point introduces some uncertainty in the application of these results to oven-rise.

Impact on mechanical properties of crumb

Gelation mainly proceeds during the cooling phase, resulting in a three-dimensional network where the swollen, yet deformable, granules are embedded into a continuous matrix of entangled amylose molecules. Such a gel is metastable and undergoes transformation during storage comprising further chain aggregation and recrystallization (retrogradation).

The heating rate during baking and possibly the post-baking cooling rate, are known to affect the process of retrogradation (Biliaderis 1991). Le-Bail and others (2009) studied different heating rates during bread baking (8, 10 and 13 °C/min obtained with oven temperatures of 180, 200, and 220 °C) and evaluated the staling rate of bread crumb through the changes in the Young's modulus and by the melting enthalpy of amylopectin. they concluded that breads baked at 8 °C/min exhibited a staling rate almost twice as slow as the others. Patel and others (2005) also tested different heating rates in crumb (6–17 °C/min) by varying the heating mode (convective, impingement, or combined) as well as the dough size (small versus large) using an even oven temperature. Consistent with Le-Bail and others (2009), they reported lower enthalpies of amylopectin recrystallization and lower incidences of bread firmness

when breads were exposed to slower heating rates and longer times above the melting temperature of native starch. This was related to the extent of amylose leaching and the enhanced associations of amylose inside and outside the granules, as evidenced by lower levels of soluble amylose.

Crust formation

Because of exposure to high temperature, crust differs from crumb in many respects: it is colored, but it is also dry, dense, and with elongated or small cells; all these aspects confer more cohesion and hardness to the crust material (Vanin and others 2009).

Dehydration and its effect on reactions in and mechanical properties of the crust

Water content and thickness of the crust depend on many factors relating to water evaporation; among them the initial porosity of the dough, duration of baking, intensity of drying at the dough surface, and the temperature at which cells collapse (Jefferson and others 2006). The crust is dense despite its lower water content because the cells are few, small or elongated. When the crust–crumb ratio is expressed in terms of its mass, it is high, between 1 and 2 (Le-Bail and others 2011). Note that water loss, and hence weight loss, is an essential part of crust formation and, therefore, manipulating the oven conditions to reduce water loss will unavoidably change the characteristics of the crust.

The extent of starch gelatinization is governed by water content and temperature history (Fukuoka and others 2002). The fast evaporation of water at the dough surface due to high temperature impedes the full gelatinization of starch in the crust (Figure 19.3 and Figure 19.4). Using DSC, Primo-Martin and others (2007) estimated that the fraction of starch crystallites in the crust was between 32 and 43% depending on the baking conditions; these crystallites melted at 70 °C, suggesting that during baking the less stable crystals in the crust had gelatinized (melting point of 50–60 °C).
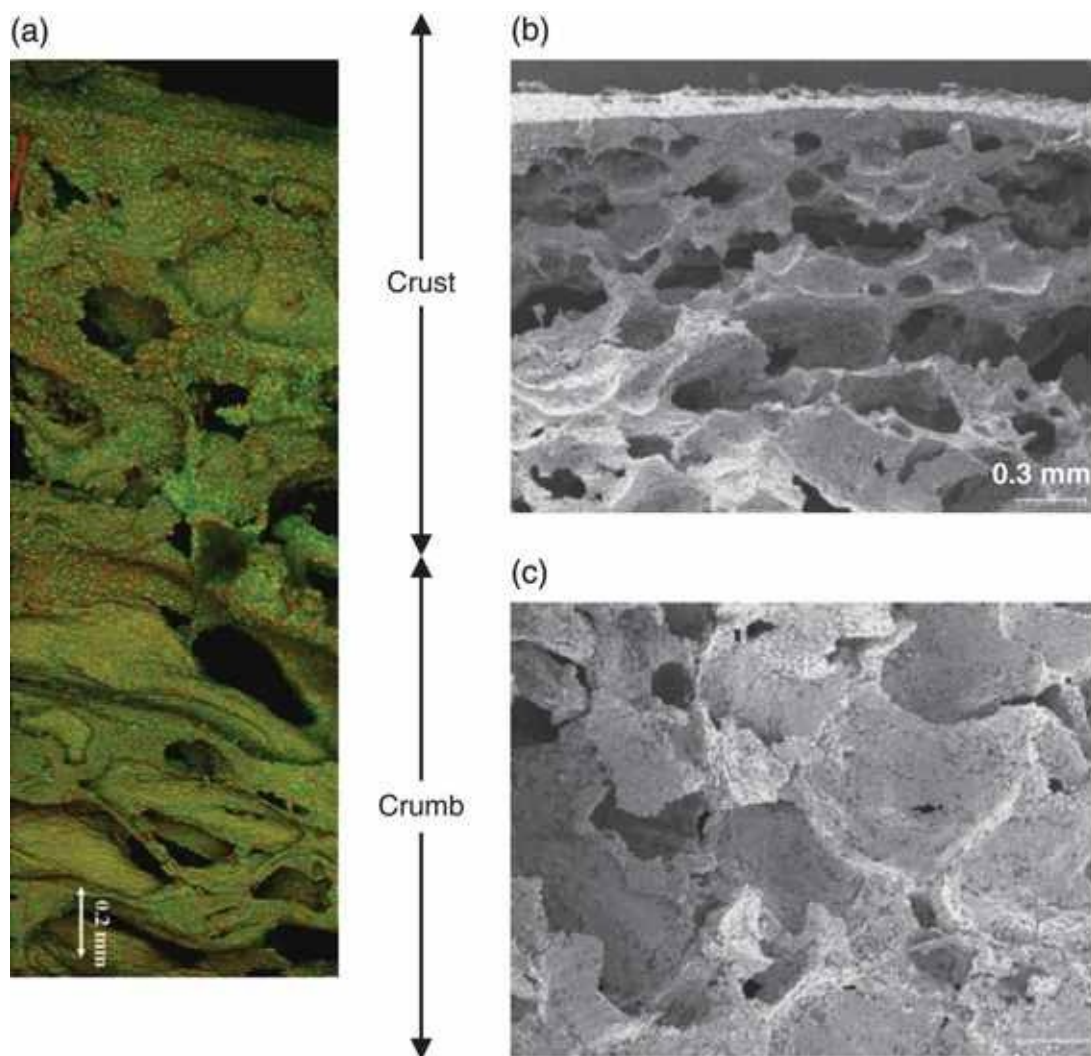
Figure 19.4 Microstructure of bread crust and crumb analyzed by (a) 3D confocal microscopy (Primo-Martin and others 2007. Reproduced with permission of Elsevier.) and (b, c) by SEM at 50× magnification (Datta and others 2007. Reproduced with permission of Elsevier). Crust at the top of image (a) is composed of a continuous protein network (stained in red) and a discontinuous starch network (stained in green), with a preserved granular shape. When moving from the outer crust towards the crumb an increased extent of starch gelatinization is observed and only remnants of granules are recognized. SEM samples (b) crust, (c) crumb were baked with microwave heating combined to with infrared.

The decrease in water content, rather than partial starch gelatinization, is mainly responsible for the increase in viscosity in the surface layers during baking of bread dough (for example, Vanin and others 2010, 2012). Similarly, protecting dough samples with paraffin oil to prevent dehydration allowed continuous expansion until 100 °C, whereas with dehydration, expansion ceased well before a temperature of 100 °C was reached (Le Meste and others 1992). This increase in viscosity may govern the cessation of the oven-rise if the viscosity increase occurs early during baking (see previous section about cell expansion).

Rigidity, together with thickness, is a crucial feature of the crust as it helps to maintain the whole alveolar structure. Many observations are consistent with this conclusion; for example: (i) when crust is thin and still flexible such as in part-baked bread loaves, collapse of the loaves as a whole is often observed during cooling together with the formation of side riddles; (ii) the lowering of pressure measured in loaves during post-baking cooling is associated with a reduced capability of the product boundaries to deform (Grenier and others 2010). In fact,

the condensation of vapor upon cooling first occurs in the peripheral layers of dough. In this latter study, it was not immediately counterbalanced by a decrease in pore volume locally, meaning that the peripheral layers were not very deformable; neither was it immediately counterbalanced by an enrichment in gases from the surroundings, especially the air from the outside, meaning that the peripheral layers were not very permeable to gases (more details are given later).

Low water activity (optimal between 0.4 and 0.8) and high temperatures (commonly above 105 °C as mentioned earlier) accelerate the Maillard reaction in the crust. Highly reactive compounds are initially produced which then polymerize, yielding brown products. Browning is linearly correlated to water loss (for example, Wahlby and Skjoldebrand 2002). Finally, some of the desired flavors and aromas of bread – among which are 2-acetyl-1-pyrroline, 4-hydroxy-2,5-dimethyl-3(2H)-furanone, 2,3-butanedione, methional, (E)-2-nonenal, methyl-propanal, and 2- and 3-methylbutanal for bread crust – are also produced, mainly by the Maillard reaction (Poinot and others 2008). The transfer of these compounds towards the oven atmosphere or the crumb during baking has been recently studied (Onishi and others 2011).

Role of steam injection on the crust formation

Steam injection delays the evaporation of water at the dough surfaces by condensation of water from the oven atmosphere onto the dough surface. Condensation proceeds as long as the crust temperature is below the dew point temperature of the oven atmosphere, which in practice occurs during the first minute of baking under classical operating conditions. The rate of increase in crust temperature will then level out as it approaches the dew point temperature, marking the point where condensation changes to evaporation (Wiggins 1998).

When baked in a dry atmosphere, bakery products have a dull surface appearance and a rather harsh color. It is commonly believed that water condensation also permits full starch gelatinization at the surface, favoring the formation of a glossy crust. However, most microscopic studies did not find evidence of starch gelatinization at the surface of bakery products. High levels of injected steam might be required for this (Altamirano-Fortoul and others 2012). Another alternative mechanism, valid for biscuit or cookie dough, is the leaching out of sugars at the surface by condensed water droplets which later form a glassy coating with gloss (Wade 1988).

It is important to understand, however, that the intensification of heat transfer at the dough surface by increasing the amount of steam injected into the first part of the travelling oven, is known to reduce the total thickness of thin bakery products like semi-sweet biscuits and cream crackers (Wade 1988).

Cell expansion in the crust; effect on permeability of crust to gases

Because of the proximity of the boundary with the oven air, gases easily escape the superficial dough layers and the vapor pressure remains close to the atmospheric pressure (also see pressure profiles calculated by Zhang and Datta 2006). Additionally, the loss of extensibility of cell walls would be expected to be more rapid, mainly because of the great reduction in

water content. Thus, one explanation of the smaller size of cells in the crust than in the crumb ([Figure 19.4](#)) is that the forces favoring expansion are not sufficient for cell expansion. The full mechanism underlying cell expansion in crust warrants in-depth study, however; for instance, Altamirano-Fortoul and others (2012) reported higher porosity in the superficial layers of bread dough when starch granules remained intact. Moreover, the surface layers cannot deform fast enough to accommodate the core expansion (see section about cell expansion). This leads to squeezing, elongation of cells located near the surface, as observed dynamically during baking (Whitworth 2008).

It is well known that the permeability of a porous medium is affected by the pore fraction and structure. Permeability to gases developed in the surface layers during baking is low; as a result, it limits water migration during baking (Wählby and Skjöldebrand 2002; Hirte and others 2010; Baik and Chinachoti 2000) and favors pressure build-up (Grenier and others 2010) with possible impacts on the local development of the alveolar structure (see previous section on cell expansion). Although receiving a renewed interest, gas permeability in bakery products has been the object of very few studies so far, and beyond this basic need for understanding, searching for ways to control the setting up of this property during baking would also be of industrial relevance (see more details later). Permeability of bread crumb was directly related to porosity (0.1–0.6), whatever the water (15–50% wb) and fat (2–8%) contents (Goedeken 1993). Chaunier and others (2008) reported differences by a factor of almost 10 between bread and brioche crumbs exhibiting the same porosity; this was explained by the size of connections (holes) in the walls separating cells, large-sized for bread and tiny for brioche. From these studies, the permeability of typical crumb (> 80% of porosity) was estimated at around 3×10^{-10} m^2, and of typical crust (40% of porosity) around 10^{-12} m^2. Hirte and others (2012) estimated the permeability in the crust of crispy rolls to water vapor as being 5×10^{-9} g/(m s Pa).

Factors affecting the crispiness of bakery products, and bread crust

In cookies, crispiness develops with the setting of a sponge structure (open pores) at the final stage of baking (Piazza and Masi 1997); the mechanisms governing the opening of pores have been described in a previous section.

Several studies also found a relation of crispiness to water content or water activity (Roudaut and others 2002; Primo-Martin and others 2006). At low water contents, gelatinized starch and gluten matrices are in a glassy state making cell walls more prone to fracture (Stokes and Donald 2000). Crispiness of biscuits, cookies, and crackers can be preserved easily by packaging which keeps their water activity constant. However, maintaining a low water activity in bread crust is not possible because water migrates from the wet crumb to the dry crust, causing a loss of crispiness within a few hours (Hirte and others 2010).

In an interesting study, lower water contents in the crust at the end of baking were obtained by using flour with lower protein content, or by hydrolyzing proteins in the dough surface layers by the application of a protease onto the dough surface at the end of proving (Primo-Martin and others 2006); in turn, these lower water contents at the end of baking permitted longer retention of crispiness.

Increasing the crust permeability to water vapor would also provide an effective way to increase crispiness retention during storage by up to 1 day (Hirte and others 2010), with only a small impact on the amount of water lost by the inner crumb (Hirte and others 2010) or on crumb dryness (Hirte and others 2012); this remains valid for permeability values lower than 8×10^{-9} g/(m s Pa).

The end point of baking

The completion of the baking process is in general judged by two properties of the product: its color and its moisture for low-moisture products, and for high-moisture products, its color and the completion of starch gelatinization at the core (often associated with a temperature exceeding 98 ºC). Satisfactory baking conditions optimize the thermal gradient through the product. Attempts to reduce baking times by increasing oven temperatures increases the darkness of the outer layers, and affects the crust–crumb ratio of high-moisture products (Wade 1988; Ahrne and others 2007), while producing an unbaked core in bread (Ahrne and others 2007) and paler inner crumb in biscuit (Wade 1988). High heat transfer at the surfaces also hastens the setting of the outer layers and limits the extent of the oven-rise because the gases do not have enough time to complete their potential for expanding cells (Wade 1988; Wagner and others 2008). Long baking durations tend, however, to decrease crumb softness (Cauvain and Young 2001).

The hottest temperatures (300–350 ºC) are used for cracker products containing little or no added sugars. Semi-sweet biscuits and sugar-containing crackers are baked at lower temperatures (250 ºC) and the short and soft doughs at about 200 ºC (Wade 1988). Bread doughs are baked between 200 and 275 ºC (Zanoni and Peri 1993; Sommier and others 2005; Ahrne and others 2007), but at much lower temperatures (160 ºC) for part-baking purposes. Oven temperatures during cake baking are in the range 150–200 ºC (Baik and others 2000a).

The time taken to achieve a satisfactory baked product depends to a considerable extent upon the properties (especially thickness) of the product itself. A thin biscuit such as a soda cracker can be baked satisfactorily in a time of about 2 min whereas a thicker product such as large short bread or wire-cut cookie may take 10 min or more. Microwave heating could be combined with conventional baking to homogenize the final water content rather than reduce the baking time (Ahmad and others 2001). Baking durations for bread loaves range from 10 to 30 min; baking time is reduced to 7–10 min for crispy rolls with the shortest baking times being achieved with the highest oven temperature of 220 ºC in a deck oven (Le-Bail and others 2010) or by using combined microwaves and airjet impingement (Datta and others 2007). Baking times of 10–15 min are required for 200 g dough depending on the oven temperature in the range 200–260 ºC (Ahrne and others 2007); 30 min for 350 g dough with oven temperatures of 200 ºC (Zanoni and Peri 1993) or 235–275 ºC (Sommier and others 2005); and 35 min for 600 g dough at 225 ºC (Thorvaldsson and Sköldebrand 1998).

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20

Packaging and Shelf-life Prediction of Bakery Products

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Introduction

Bakery products have been a basic part of the human diet for centuries with bread being the staple product consumed daily by most of the population. Bakery products are popular and appealing due to their nutritional, sensory, and textural characteristics.

A wide variety of bakery products is produced, such as cakes, crackers, and cookies. Common characteristics of all bakery products are that they contain cereal flour as their basic ingredient, and require baking as part of their manufacture.

The quality features of bakery products start to deteriorate immediately after baking, however, leading to staling, loss of moisture and flavor, and a limited shelf-life. During recent decades, due to consumers' needs and demands as well as changes in the way food products are manufactured, distributed, and retailed, a great variety of bakery products have been developed together with alternative or novel methods for their production and preservation.

For these reasons, research has been focused on the development of advanced packaging and preservation technologies and techniques for bakery products. Inherent overall product quality, as well as environmental storage conditions, influence the characteristics of bakery products and hence affect their acceptance. Thus packaging materials, methods, and conditions have been investigated for different bakery products, as well as the methodology for the estimation and prediction of their shelf-life (Matz 1989; Kulp and others 1995; Laaksonen and Roos 2000; Bhattacharya and others 2003).

Classification of bakery products

Bakery products comprise an enormous variety (in size, shape, color, texture, taste, and flavor) of goods which can be either classified according to their formula (mainly sugar content or leavening type), pH level and moisture content, or water activity (a_w). Therefore they can be categorized (Table 20.1) into:

- unsweetened (bread, rolls, crackers, pizza base, crumpets, bagels), sweet goods (cakes, biscuits, cookies, muffins, pancakes, doughnuts, waffles), and filled goods (fruit and meat pies, pastries, sandwiches, cream cakes, pizza and quiche);
- leavened with yeast (most commonly *Saccharomyces cerevisiae*) or chemical agents (baking powders made up most commonly of baking soda, acid salts, and inert fillers), or unleavened (without fermentation or gas-producing agents) products;
- high acid (pH < 4.6), low acid (pH > 4.6 and pH < 7), and nonacid or alkaline bakery products (pH > 7).

Table 20.1 Classification categories for bakery products

Product type	Leavening type	pH	Moisture a_w
Unsweetened Sweet Filled	Unleavened Yeast raised *Saccharomyces cerevisiae* Chemically leavened Baking powders	High acid pH < 4.6 Low acid pH = 4.6–7 Non acid pH > 7	Low moisture content a_w < 0.6 Intermediate moisture content a_w = 0.60–0.85 High moisture content a_w > 0.85

For the scope of this chapter, bakery products are classified according to Smith and Simpson (1995) based on their moisture content as:

- low moisture (a_w < 0.6) products (cookies and crackers);
- intermediate moisture (a_w > 0.6 and a_w < 0.85) products (soft cookies, doughnuts and danish pastries); and
- high moisture (a_w > 0.85) bakery products (bread, cakes, pies).

Low moisture products are usually fragile and highly hygroscopic and are characterized by their crisp or crunchy texture. Under proper packaging and storage conditions, they can be preserved for a long period. Intermediate and high moisture bakery products exhibit a pliable or creamy texture and a shorter, and in some cases very limited, shelf-life. The shelf-life of low and intermediate moisture bakery products is usually limited by physical (moisture gain or loss and staling) and chemical (rancidity) factors; while microbiological spoilage by bacteria, yeast, and molds is the main concern in high moisture products (Smith and Simpson 1995; Smith and others 2004).

Characteristics of bakery products

The main characteristics of the most important bakery products are summarized in the following sections.

Bread

Bread is characterized by a dry thin crust (moisture content 12–17%), that encloses a soft, sponge-like cellular structure (moisture content 35–40%). The basic ingredients required for the production of bread are flour, yeast, salt, and water. Other ingredients may also be used such as fat, sugar, milk or milk substitutes, oxidizing agents, enzymes, dietary fibers, protein products, surfactants, hydrocolloids, and/or preservatives. Each of these ingredients may serve specific functions in the production of bread, the most important of which are easy dough handling, improved texture or sensory characteristics, higher nutritional value, and longer shelf-life (Autio and Laurikainen 1997; Cauvain and Young 2006).

Cakes

A great variety of cake products exists with a broad range of formulations. The two basic categories of cakes – foam and shortened – are distinctly different in their preparation and characteristics. The shortened-style cake (for example, pound cake, yellow cake, chocolate cake) has a crumb structure derived from a fat–liquid emulsion that is created during batter processing. Foam-style cakes (for example, angel food, sponge, chiffon) depend on the foaming and aerating properties of eggs for their structure and volume.

In general cakes contain high levels of shortening, sugar, eggs, and milk. They are characterized by a sweet taste, a short and tender texture, and pleasant flavors and aromas.

The total moisture content of cakes 10–20% lower compared than that of bread. They do have a crust, though somewhat thinner than the average crust on breads, and a less well-defined cellular structure. Both moisture and product density have a major impact on cake eating quality. Lower moisture contents yield firm, dry-eating products, while more dense cake products tend towards pastry eating characteristics (Pyler 1988; Cauvain and Young 2006; Hui 2006; Lai and Lin 2006a).

Biscuits and cookies

Biscuits are small baked products of many shapes and sizes made principally from flour, sugar, and fat. After baking they may be coated with chocolate, sandwiched with a fat-based filling or have other pleasantly flavored additions. They can be divided into two groups. Those with very low moisture content and those containing, for example, caramel, jam or fruit paste, that have higher moisture content. Most biscuits fall into the first group and typically have a moisture content of < 4%. When packaged in moisture proof containers, they have a long shelf-life, perhaps 6 months or more.

Biscuit dough can be either hard or soft and the difference is determined by the amount of water required to make the dough. Hard doughs have high water and relatively low fat (and sugar) content and the dough is tough and extensible. Soft doughs contain much less water,

relatively high levels of fat and sugar and exhibit very low extensibility. Biscuits made from soft dough are of the soft eating types and are often referred to as "cookies" (Manley 2000; Hui 2006; Lai and Lin 2006b).

Crackers

Crackers are dry (moisture content 2–3%), thin, crisp bakery products that may be leavened or unleavened and are made in various shapes. A cracker makes a cracking or snapping noise. These products may range from those with a close similarity to some semisweet machine-cut cookies to fermented, crisp, non-sweet, laminated types. Among the fermented products, the soda cracker or saltine cracker and the cream cracker are the most representative.

The basic ingredients in cracker production are wheat flour, fat (or shortening), salt, leavening agents (yeast, chemical leaveners, or a combination) and water. Other minor ingredients include sweeteners, emulsifiers, malt flour or enzymes, acidulants for chemical leavening, whey, egg, flavorings, and dough conditioners (Hui 2006).

Storage – quality characteristics and deterioration during storage

The shelf-life of bakery products can be as short as a few hours or as long as a year, depending on the type of product and the storage and packaging conditions. As mentioned before, the shelf-life of bakery products is limited by physicochemical or microbiological factors and is highly dependent on their moisture content.

Bakery products with low moisture content

Products with low moisture content, such as biscuits, are susceptible to loss of crispness and sensitive to water vapor interchanges (moisture) and oxygen reactions. Prolonged exposure of these products to ambient storage conditions leads to water absorption from the atmosphere into the product's matrix, making it lose crispness and become soft, soggy, and consequently less acceptable to most consumers. The critical moisture level for loss of crispness varies between 4 and 6%.

Moisture absorption by dry bakery products, such as biscuits and cookies, may also lead to a change in product dimensions. The usual form of change is an increase in size, commonly diameter or length, although an increase in thickness is also possible. Such dimensional changes are more prominent for coated products and may lead to cracks in the coating.

Many biscuits and crackers are also susceptible to the formation of cracks and splits without being subjected to any mechanical distress. As soon as baking is completed and they begin to cool, they exhibit lower moisture content at their edges compared to that at the center. Gradually moisture moves from the moist center to the drier parts of the product and stresses are developed within the product, causing the product to break. The cracks often develop along lines of inherent weakness within the product, both macroscopic and microscopic. In round products, these cracks are often radial, while in products like crackers more randomly distributed cracks may occur (Cauvain and Young 2000).

Since these products also contain high fat levels, they can also exhibit rancidity phenomena when exposed to moisture and the atmosphere, which can be readily detected by taste and odor even at fairly low levels. Rancidity can either be oxidative or hydrolytic. Oxidative rancidity results in the breakdown of unsaturated fatty acids by oxygen through an autolytic free-radical mechanism. Consequently, malodorous aldehydes, ketones, and short-chain fatty acids are formed. Hydrolytic rancidity, unlike oxidative rancidity, occurs in the absence of oxygen and results in the hydrolysis of triglycerides and the subsequent release of glycerol and malodorous fatty acids. This type of rancidity is enhanced by the presence of moisture and endogenous enzymes, such as lipases and lipoxygenases. These enzymes catalyze the oxidation of unsaturated fats, producing peroxides and heat-stable compounds that survive the baking process. Fruits and nuts used in many bakery products are also susceptible to oxidation in the presence of oxygen. Light is also detrimental to colors or causes oxidation of fats leading to rancidity and undesirable off-flavors. Other deteriorative reactions that may possibly occur during storage are the degradation of carotenoids and other pigments (causing product discoloration), and non-enzymatic browning. For each of these chemical reactions, the water content of the food is of primary importance (Coles and others 2003; Hui 2006).

Bakery products with intermediate or high moisture content

These products contain hydrated starch and are prone to staling. Staling is a complex process that starts soon after baking and involves several physicochemical changes. These are mainly related to an increase in crumb firmness and a resulting loss in product freshness, which is further linked to a loss of eating quality due to color, flavor, or texture deterioration (Lebesi and Tzia 2011). A predominant role has been assigned to starch retrogradation, as starch is a major component of the system, which involves the progressive association of gelatinized starch segments from an amorphous to a crystalline form (a more ordered structure), the latter binding considerably less water than the former (Zobel and Kulp 1996). This change leads to a rapid hardening and to shrinkage of the starch granules with consequent development of crumbliness and loss of texture. The general consensus is that amylopectin retrogradation contributes significantly to staling or undesirable firming of bread and other starch-based products, whereas a less important role in staling is recognized for amylose. Furthermore, loss and/or transfer of moisture from one constituent of the crumb to another is generally accepted as a contributing factor in staling, possibly being responsible for the perceived dryness of stale products. It should be noted that the moisture transfer is independent of the moisture content of the inner portion of the product. Whether staling involves the dehydration of gluten or starch has been studied extensively, but is still unclear. However, most evidence suggests a gluten to starch transfer of water as the starch crystallizes (Gray and Bemiller 2003).

Bakery products with a crust (mainly bread and cakes) tend to dry out rapidly as water migrates from the crumb, and acquire a firmer texture and a drier, harder eating character. The crust, however, tends to become rubbery or soggy. The rate at which these changes occur depends on the storage conditions, the thickness of the crust, and the ratio of crust to crumb in the product (Robertson 1993; Barcenas and others 2003; Hui 2006).

Moisture migration is of particular importance in composite bakery products. These consist of a dough component and one or more filling components baked together as in the case of fruited cakes, or those prepared by introducing the filling into the already baked product as in the case of sandwich biscuits. These products contain components with very different appearances, textures, eating characteristics and moisture contents. When placed in contact with one another, moisture diffuses from the wetter to the drier phase to achieve equilibrium, leading to irreversible changes in the texture, sensory, and microbiological quality of the product, and to the reduction of its shelf-life. Moisture diffusion rate depends mainly on the water activity level of each component, and increases with greater difference in water activity (Labuza and Hyman 1998; Cauvain and Young 2000).

In intermediate moisture products (a_w = 0.6−0.85), osmophilic yeasts and molds are the predominant spoilage microorganisms; while in products with the highest moisture (a_w = 0.94−0.99), almost all bacteria, yeasts, and molds are capable of growth.

In un-preserved bread a shelf-life of 3−4 days is usually expected. As well as the repellant sight of visible fungal growth, fungi (mainly yeasts and molds) are responsible for off-flavor formation and the production of mycotoxins and allergenic compounds, which may be formed even before growth is visible. In wheat bread, *Penicillium commune, P. solitum, P. corylophilum* and *Aspergilllus flavus* dominate, whereas *P. roqueforti, P. corylophilum*, and to some degree also *Eurotium* species are dominant in rye bread. Also yeasts commonly

known as chalk molds are important spoilers of bread. The most important of these species is *Endomyces fibuliger*.

Bakery products with high moisture content may also develop bacterial infection, the most common of which is "ropiness" caused by *Bacillus subtilis*, a spore-forming bacteria. This microorganism is usually present in raw ingredients (for example, flour, sugar, and yeast), survives the baking process, germinates upon cooling, and grows under both aerobic and anaerobic packaging conditions. Ropiness is usually detected by the discoloration and stickiness of the crumb and the development of a characteristic odor and taste in the loaf (Nielsen and Rios 2000; Smith and others 2004).

Packaging

Packaging plays a very important role in delivering safe, wholesome, and attractive foods to customers. It includes the processes and materials employed to contain, handle, protect, and transport a product. Packaging may also attract customer attention, assist in promotion, provide traceability, enable machine identification (barcodes), impart essential or additional information, and help in utilization.

Packaging can be categorized in to three main groups:

- "Primary" or "sales" packaging is in direct contact with the contained product. It provides the initial and usually the major protective barrier and forms a sales unit for the user or final consumer, for example, a box containing biscuits.

- "Secondary" or "grouped" packaging contains a number of sales units, for example, a cardboard outer containing a number of boxes of biscuits.

- "Tertiary" or "transport" packaging is used to group secondary packaging together to aid handling and transportation and to prevent damage to the products, for example, the pallet and shrink-wrap used to transport a number of cardboard outers containing boxes of biscuits.

The most important functions of packaging (Table 20.2) are summarized here (Robertson 1993, 2006; Emblem 2000).

Table 20.2 Functions of packaging

Primary	Secondary	Tertiary
Containment Protection Convenience Storage Loading and transport	Communication Service Guarantee	Additional functions

Containment: This is the most basic function of packaging as food products must be contained before being transported from one place to another. The kind of packaging needed to contain a product depends on the physical and quality characteristics of the product, since products come in many shapes and sizes and react in different ways to their surroundings and environment.

Protection: During their journey throughout the supply chain, food products may be exposed to various environmental or mechanical hazards such as contact with light, high or low temperatures, solar radiation, moisture, gases, odors, microorganisms, insect and rodent dust and dirt, or exposure to shocks, shaking, vibrations or compressive forces during transport, handling, and storage operations. Therefore packaging must provide a suitable barrier around the food and physical protection against these hazards. The inward and outward protective function of transport packaging primarily places demands upon the strength, resistance and leak-proof properties of the package.

Packaging must also prevent any degradation, contamination, damage or other negative

impacts from the environment and other external materials.

Convenience: Convenience includes all aspects of the movement and use of the product from the packaging line to final use and disposal. Convenience in product use is one of the major benefits of packaging, and innovative solutions can provide major points of difference from one product to another. Convenience features of modern food packaging can include the ease of opening and, if relevant, reclosing.

Two other aspects of convenience are important in package design: (i) reduction of the unit output from industrial production to a manageable, desirable "consumer" size; and (ii) the shape of the primary package so it is convenient for consumers and can be efficiently built it into secondary and tertiary packages.

Storage: Most food products are stored before final distribution or remain in storage in the warehouses of retail outlets before being put on the shelves. Packaging must thus also fulfill a storage function.

Loading and transport function: Packaging (mainly secondary or transport) has a crucial impact on the efficiency of transport and the handling of food products. Therefore packaging should be designed for easy and safe handling, lifting, moving, space-saving, and stowage.

The loading and transport function places requirements upon the external shape of the packages, the mass of the goods accommodated inside and the convenient use of packaging aids. Where possible they should be tailored to the dimensions and load-carrying capacity of standard pallets and containers. The shape and strength of the package required for stowing goods should be such that they may not only be stowed side by side, leaving virtually no voids, but may also be stowed safely one above the other. These attributes are closely related to the protective function of packaging.

Communication: Packaging can also enable or promote the sales process and make it more efficient. In modern self-service supermarkets especially, messages are communicated using packaging with distinctive branding and labeling. The consumers' attention can be attracted by packaging with enticing colors, shapes, sizes, and graphics, which will affect their choices.

Even if supplementary information is available at the point of sale, once the product is purchased, packaging is usually the only way for customers to find out important information such as nutritional details, product ingredients, or instructions for use and storage.

Other communication functions of the packaging include the Universal Product Code (UPC) which can be read accurately and rapidly using modern scanning equipment at retail checkouts providing important information on the product.

The items on the package label that are required by law are:

- manufacturer's name and contact details
- name of the product
- description of the product
- weight (some foods are exempt)
- ingredients (listed in descending order of weight)
- cooking/heating instructions (if necessary)

- storage instructions
- shelf-life
- place of origin
- allergy information.

The following items are not legal requirements, but are nevertheless often included on the packaging as good practice:

- illustration of product
- price
- nutritional values of the product
- customer guarantee
- the batch-code and bar-code numbers
- opening instructions.

Services: The various items of information printed on packaging provide consumers with details about its contents and the use of the particular product. The packaging may also perform a further function once the contents have been used (for example, acting as a storage container).

Guarantee: By supplying an undamaged and unblemished package, the manufacturer guarantees that the details on the packaging correspond to the contents. The packaging is therefore the basis for branded goods, consumer protection and product liability. There are legislative requirements which demand that goods be clearly marked with details indicating their nature, composition, weight, quantity, and storage life.

Additional functions: It is important that all materials used for and on packaging comply with certain safety specifications and do not impart any undesirable or hazardous contaminants to the food. Although this attribute may seem self-evident, there has been a long history of so-called food-contact substances migrating from the packaging material into the food. Not surprisingly, food packaging materials are highly regulated in many countries to ensure consumers' safety.

Finally there are other attributes of packaging that are also important such as the extent to which the packaging materials or packaging containers may be re-used or recycled once the package contents have been consumed. Packaging materials throughout their life cycle, from raw materials to final disposal after use, should have minimal adverse environmental impacts.

A range of plastic materials mainly in the form of films, laminates, and thermoformed trays are most commonly used for the packaging of bakery products. These materials, when properly designed, provide adequate protection against moisture loss/gain or oxygen uptake, retain the taste and aroma, and are hygienic and safe for food contact. The permeability of a penetrant through a polymer depends on many factors, including the nature and structure of the polymer, thickness of the film, size and shape of the penetrant, pressure, and temperature. The dimensions of the package for a given weight of food can also have a significant influence on its shelf-life. A spherical shape minimizes the surface area of the

package (and thus the quantity of moisture or oxygen that will permeate the package walls) but it is not of practical use. Thinner packages have a greater surface area to volume ratio and thus require plastic materials with better barrier properties to ensure the same shelf-life than if the same quantity of product was packaged in a thicker format.

For different quantities of the same product, packaged in different-sized packages using the same plastic material, the smallest package will have the shortest shelf-life as it inevitably has a greater surface area per unit of volume.

Apart from these considerations, polymer materials are considered suitable for packaging bakery products due to additional properties such as machinability, printability, and cost effectiveness.

The basic features of a package intended to contain bakery products relate to:

- water vapor permeability
- oxygen exchange from within and outside
- aroma impermeability
- resistance to seepage of fats and oils
- protection against deteriorative visible and ultraviolet radiation
- good printability and appearance
- physical, mechanical protection to the products against shocks, crushing, and vibrations
- compatibility and safety.

Bakery products with low moisture content

Flexible packaging materials and thermoformed plastic trays are the most common materials used for these products. In order to provide the necessary mechanical protection to the product, end-fold style portion packs or pillow packs puffed up with gas are used to prevent breakage during transport and retail handling. Often individually wrapped packs are used to eliminate the hygiene factor risks since products do not come in to direct contact with the external environment.

Flexible packaging materials are commonly used as wrappers or pouches (either pre-formed or form-filled). Cellophane is the oldest flexible film used, providing excellent gas barrier properties and heat sealability, while coated cellophane offers an excellent moisture barrier, heat sealability, and gloss. However, cellophane is an expensive material and it has often been replaced by newer materials.

High-density polyethylene (HDPE) and polypropylene (PP) pouches are suitable for short-term storage and perform well in machines. For longer storage life, biaxially oriented polypropylene (OPP) liners are beneficial for reducing water vapor ingress. Plain OPP films are economical but generally require a heat seal coating on the sealing side to improve sealability and therefore are used for less demanding applications. For higher quality products, duplex OPP or OPP combinations (pearlized or metallized) such as OPP/polyethylene (PE), OPP/polyethylene terephthalate (PET) are used. Laminates such as cellophane/PE, coated foils, and metallized polyester/PE are also used. If a superior oxygen

barrier is required, acrylic-coated OPP is used, and sometimes one side is coated with polyvinyl chloride (PVC)/polyvinylidene chloride (PVdC) co-polymer rather than acrylic. Also acrylic and PVC/PVdC copolymer-coated OPP films provide a superior flavor and aroma barrier compared to that of uncoated OPP.

Today, most biscuits are packed in flexible laminates of composite structures, where every component fulfills a specific function. These laminates have desirable properties such as moisture barrier, gas barrier, heat sealability, printability characteristics, high production, and overall economy (Robertson 1993; Coles and others 2003). The different types of plastic films and their uses are described in Table 20.3:

Table 20.3 Different types of plastic films and their uses

Material	Properties
Cellophane	Glossy transparent film, odorless and tasteless Tough and sharp resistant, but it tears easily Not heat sealable, low permeability to gases, oils, greases, bacteria and water
Low density polyethylene (LDPE)	Tough, slightly translucent, odor-free, heat sealable and inert material that shrinks when heated Good tensile strength, burst strength, impact resistance, and tear strength Excellent moisture barrier, with relatively high gas permeability, sensitivity to oils and greases, and poor odor resistance Less expensive than most films and so widely used
High density polyethylene (HDPE)	White, translucent appearance; stronger, thicker, less flexible, and more brittle than LDPE Chemical resistance superior to LDPE with better resistance to oils and greases Excellent moisture protection and decreased gas permeability compared to LDPE film, but is much more opaque Heat sealing is considerably more difficult compared to LDPE film, and so bags commonly sealed with rubber ring or metal clip, particularly for very large bags
Polypropylene (PP)	Clear glossy film (ideal for reverse printing) with high strength and puncture resistant Low water vapor transmission, medium gas permeability, good resistance to greases and chemicals, good abrasion resistance, and high temperature stability Susceptible to oxidative degradation at elevated temperatures Biaxially oriented PP film has superior and improved moisture barrier properties compared to plain PP OPP films have an insufficient gas barrier but this can be overcome by coating with PVC or PVdC co-polymer OPP films often have a stiff feel and tend to crinkle audibly
Coated films	Films coated with other polymers or aluminum to improve barrier properties or to enable them to be heat sealed
Laminated films	Two or more films glued together Lamination improves the appearance, barrier properties, or the mechanical strength of a package Aluminum foil is widely used where low gas, water vapor, odor, or light transmission is required

Mechanical protection is generally provided either by placing the product in a protective rigid container such as a carton of appropriate thickness, or by packaging the product tightly together. In the case of moisture sensitive bakery products, the carton is overwrapped with a film which can provide a good barrier to moisture vapor. A further option is to place, for example, biscuits or cookies inside thermoformed plastic trays. Thermoformed plastic trays

of polystyrene or PVC with multiple cavities are commonly used. They are closed with a snap-on lid, overwrapped or shrink-wrapped or sealed with a lidding material which provides the required protection from moisture vapor and oxygen. This enables good presentation as the products are accurately aligned in the tray (Robertson 1993, 2010).

Bakery products with intermediate or high moisture content

Packaging materials suitable for bakery products of intermediate/high moisture content should ideally:

- maintain adequate shelf-life and protect the bakery products until staling occurs
- be an adequate moisture barrier
- protect the shape of the product
- offer good printability and appearance
- run on automatic machinery
- be strong
- be inexpensive.

Many bakery products, especially of high moisture content, are marketed fresh and are stored at ambient temperature. However, they can also be stored under refrigerated or frozen storage conditions to achieve a longer shelf-life. Since these products generally lose moisture to the atmosphere, a slightly water vapor-proof packaging material is needed to prevent rapid drying out, and to protect the crust from becoming soggy and mold sensitive. Protection is also required against handling and dust. The use of a moisture impermeable package would lead to internal condensation, fogging and consequently mold growth. The recommended packaging materials are preferably heat sealable waxed papers with high water vapor permeability, semi-moisture-proof cellophanes or HDPE. LDPE, LLDPE-LDPE and PP films are also used. LLDPE is linear low density polyethylene that is made by the co-polymerization of ethylene with a co-monomer. In auto-bagging machines, high slip PE resins, that is, pouches with good openability, are commonly used.

Bread is usually packaged in LDPE bags in which the end is twisted and sealed with a strip of adhesive tape, a plastic clip or wire ties. Some speciality breads, such as French and Italian breads, may be packaged in LDPE bags perforated with small holes which allow moisture to escape and thus retain a crisp crust. Several hole sizes and hole densities are available, depending on the particular product and its surface area to volume ratio (Pagani and others 2006). Cakes and other relative products have similar packaging requirements to those of bread and, in addition, require the package to be rigid enough to protect them against physical damage. Films of PVC, PP, cast polypropylene (CPP), thermoformed containers of polystyrene (PS), and cellulose acetate are generally used (Kumar and Balasubrahmanyam 1984; Robertson 1993; Coles and others 2003).

In order to improve microbial safety during storage and prolong the shelf-life of bakery products, the use of modified atmosphere packaging (MAP) is often recommended. MAP can preserve the freshness of many food products, and improve food safety under certain conditions (Farber and others 1990). This technology has been particularly effective in chilled short shelf-life, low-acid foods, especially minimally processed and highly perishable or semi-

perishable foods. It is applied to fresh produce and prepared foods such as vegetables and meat products as well as to bakery products to improve shelf-life and quality retention (Fabiano and others 2000). The recommended proportion of gases for bakery products ranges from 20 to 50% CO_2 (against the growth of molds such as *Penicillium* and *Aspergillus*) and 80 to 50% N_2 (increased inertia), respectively (Kotsianis and others 2002).

Packaging films commonly used with MAP in bakery products are laminated or flexible films used as lidding materials, and semi-rigid plastics as containers (Crosby 1981; Ooraikul 1991). The most important characteristic of the materials is to prevent the escape of inert gases from the package (Hastings 1998).

The basic criteria for the selection of these materials are:

- permeability to fixed-gases
- water vapor and oxygen permeability
- sealability characteristics
- ability to be thermoformed
- clarity and anti-fog properties
- weight and strength.

Commonly used flexible plastic laminates are produced from PE, PP, polyamide (PA/nylons), PET, PVC, PVdC, and ethylene vinyl alcohol (EVOH). Rigid and semi-rigid structures are commonly produced from PP, PET, unplasticized PVC, and expanded PS (Yam 2009; Coles and Kirwan 2011).

Other packaging techniques alternatively used include the incorporation of oxygen scavengers/absorbers and ethanol. When an oxygen scavenger is used inside the packaging, oxygen is not completely removed, but the growth of molds and the oxidative changes that can reduce the sensory quality of bakery products are effectively controlled. A range of oxygen scavenging substances are used which can act rapidly or slowly, with moist or dry foods, or can have a dual effect such as oxygen absorption and carbon dioxide production (Harima 1990; Seiler 1998). PVdC coated nylon, polyester, LDPE, PP, EVOH, and PS are examples of flexible packaging materials used together with some sort of active sachet.

Ethanol in combination with gas packaging has been shown to increase the shelf-life of bakery products due to its antimicrobial effect (Powers and Berkowitz 1990; Seiler 1998). The growth of molds, yeasts, lactobacilli, and other microbial contaminants is retarded and the rate of staling is also reduced. Ethanol may be added to the packaging atmosphere by an ethanol vapor generator consisting of ethanol absorbed or encapsulated in a carrier material and enclosed in polymer packets. From such a packet, ethanol is released into the packaging atmosphere (Nielsen 2004). Like oxygen scavengers the major difficulty in their use is to persuade consumers to accept the presence of a sachet in the pack. In addition, ethanol may cause the development of off-flavors and off-odors inside the package (Seiler 1998).

The shelf-life of bakery products

Factors affecting the shelf-life of bakery products

Food quality is generally defined as the set of characteristics that allow the differentiation of each particular product, and determines its acceptability to the consumer or user. This includes external factors such as appearance (size, shape, color, gloss, and consistency), texture and flavor, and internal (chemical, physical, microbial, and functional characteristics). It is a dynamic situation that usually leads toward a declining quality (with the exception of certain foods such as wine or cheese, where their quality can improve under correct maturation or aging). For this reason, most foods and beverages have a finite sustainability and shelf-life before they become unacceptable. The time from production until they lose an acceptable level of eating quality, is referred to as shelf-life (Robertson 2010).

More specifically, shelf-life is defined as the time during which the food product will (Kilcast and Subramaniam 2000):

- remain safe;
- retain its sensory, chemical, physical and microbiological characteristics at acceptable levels;
- comply with any label declaration of nutritional data, when stored under the recommended conditions.

The most important parameters affecting the shelf-life of food products are (Kilcast and Subramaniam 2000; Steele 2004):

- raw material quality
- formulation
- processing
- water activity
- pH
- available oxygen
- nutrients
- natural microflora
- packaging
- preservatives
- storage conditions
- consumer handling.

Several approaches are suggested in the literature to extend the shelf-life of bakery products, which can be briefly summarized for the selection of proper packaging materials and conditions. These include the application of lower storage temperatures and the modification

of recipes and ingredients.

Storage temperature

As is commonly known, the reduction of storage temperature will result in the extension of shelf-life, as most deteriorative parameters (microbiological and chemical) are retarded at lower temperatures. In cakes and most other bakery products, the lower the equilibrium relative humidity (ERH) of the product, the greater will be the effect of lowering storage temperature (Cauvain and Young 2000).

Additionally, the application of refrigeration or freezing renders the production of bakery products particularly flexible and effective. Par-baked, refrigerated or frozen bakery products, and products made from frozen dough, can retain their quality for weeks or months provided that they are stored under suitable conditions. They can be stored, thawed, proofed, and baked in quantities proportional to daily demand, even by minimally skilled personnel at in-store bakeries, restaurants, institutions, and supermarkets, with limited requirements in equipment, to provide consumers with freshly baked products at any time of the day (Giannou and others 2005).

Product reformulation

The key parameters in controlling the shelf-life, especially in high moisture bakery products which are prone to microbiological deterioration, are their water activity (a_w) and pH levels. The stability and shelf-life of foods are highly dependent on their water content as it directly affects the rate of food deterioration reactions. Moisture levels can be controlled through the reduction of water and water-rich ingredients such as milk and eggs, or the use of ingredients with water-binding properties such as sugars, salts or humectants (for example, glycerol or sorbitol). This approach presupposes that the sensory and other quality characteristics of the product will not be adversely affected.

Tthe pH levels favoring microbial growth are between 5.0 and 7.5 (molds may grow at pH > 3). Therefore only those bakery products in which the acid flavor is an advantage, or can be masked by other ingredients, are susceptible to pH reduction. This can be achieved through the use of acidulants such as organic acids (for example, citric, lactic, acetic acids) or cultures of lactic acid bacteria (Cauvain and Young 2000; Smith and others 2004).

Preservatives at permitted levels can also be used to extend the shelf-life of bakery products, especially when extension cannot be achieved by other means. However, when used at high levels, preservatives may give rise to off-odors and flavors (Saranraj and Geetha 2012). Preservatives can either be chemical ingredients (such as acetic, sorbic, propionic acids and their salts) or natural (for example, from cultured products, raisins, vinegar).

Calcium and sodium propionate inhibit a broad spectrum of mold and rope organisms thus increasing the shelf-life of bakery foods. Although propionic acid has a higher antimicrobial activity, propionates are most commonly used in bakery products due to their greater solubility and odor-free characteristics. Compared to other preservatives, they minimally impact the activity of yeast, making them suitable for yeast-raised products. Calcium propionate (commonly used at the level of 0.15–0.30 g/kg), however, which is most effective at pH 5.5 or lower, may adversely affect baking powders.

As well as propionates, ethyl alcohol may be used to suspend microbial activity in fermented

products because of its ability to lower vapor pressure and therefore water activity. Additionally, ethyl alcohol can retard staling. Acetic acid and acetates (sodium acetate/diacetate) are also alternatives to propionates. Although less effective, on the same weight basis, they are less expensive and less toxic than propionates or sorbates.

Sorbates are quite effective in inhibiting mold growth, with their effectiveness increasing with greater acidity. Above pH 4.0, sorbates are more effective than sodium benzoate or sodium/calcium propionate. However, they inhibit yeast activity and decrease loaf volume. Thus they are not recommended for yeast-raised products and are often used in chemically leavened systems, or encapsulated, or sprayed on the surface of baked products, or incorporated into the packaging material. As sorbic acid is difficult to incorporate into a batter due to its low solubility, its salts (mainly potassium sorbate) are generally used (Cauvain and Young 2000; Sievert and Hoseney 2002; Smith and others 2004).

Other shelf-life extension techniques

Apart from chemical preservatives, ultraviolet or infrared irradiation, and aseptic, active or intelligent packaging have been proposed for controlling microbial growth in bakery products. Natural extracts from spices and herbs, such as essential oils and their constituents with antimicrobial properties, are also recommended for active packaging applications. These substances are released from the packaging material to the surface of the product during storage thus controlling microbial contamination.

Alternatively, several antimicrobial films have been evaluated for food packaging applications such as alpha- and beta-cyclodextrin-encapsulated allyl isothiocyanate in polylactide-co-polycaprolactone films, blends of gliadins and chitosan or hexamethylenetetramine, PE coated with antimicrobial peptides, or nisin-incorporated cross-linked hydroxypropylmethylcellulose (Nielsen and Rios 2000; Soares and others 2002; Guynot and others 2003; Gutierrez and others 2009).

Shelf-life estimation and prediction

The first and most important step for designating the shelf-life of food products is to efficiently understand and examine all the factors affecting the rates and mechanisms of degradation in a product's quality characteristics. The shelf-life of food products can be estimated either by using data from literature, based on the shelf-life of similar products on the market, or through shelf-life testing. Shelf-life testing can be done directly for products with a short shelf-life, or the testing can be accelerated (accelerated shelf-life testing, ASLT) for products with a medium or long shelf-life.

In direct shelf-life testing, food products are either stored under controlled conditions that simulate those likely to be encountered during storage, distribution, retail handling, and consumer use (if possible), or are stored under fixed storage conditions according to the type of product; typically 25 °C and 75% relative humidity are used for most products that do not require refrigeration or freezing. ASLT usually involves a limited number of experiments on the finished product under certain abuse conditions, with periodic product examination until it reaches the end of its shelf-life. This data is then used to predict the shelf-life under normal storage conditions (Mizrahi 2004; Steele 2004; Galic and others 2009).

Applying fundamental chemical kinetic principles, the rate of quality degradation (dQ/dt) can

be expressed as a function of endogenous and exogenous factors (Equation 20.1).

$$\frac{dQ}{dt} = f(C_i, E_j) \tag{20.1}$$

where:

C_i = formulation parameters

E_j = environmental factors.

The general expression used to describe the quality function $Q(A)$ of an attribute for a given product at constant temperature is (Equation 20.2):

$$Q(A) = k \cdot t \tag{20.2}$$

where:

A = the quality attribute examined

k = reaction rate constant (days^{-1})

t = the shelf-life in days, months, or years.

Depending on the order of the reactions occurring in each food, different quality functions are generated as shown in Table 20.4. However, most deteriorative reactions in foods are of zero or first order. The half-life, which represents the period of time it takes for the concentration of index A to decrease by half, is also shown (Taoukis and Giannakourou 2004; Galic and others 2009).

Table 20.4 Equations of quality deterioration and half-life for different orders of reaction

Reaction order	Quality function $[Q(A)_t]$	Half-life $[t_{1/2}]$
0	$A_0 - A_t$	$A_0/2k_0$
1	$\ln(A_0/A_t)$	$\ln2/k_1$
2	$1/A_0 - 1/A_t$	$1/(k_2 \cdot A_0)$

A_0 = the initial value of a quality attribute; A_t = the value of A at end of shelf-life.

This analysis assumes that the environmental factors remain stable. In real food systems, however, these are constantly changing and can influence the rates of reactions occurring within the system. Of these parameters, temperature has the strongest impact and therefore should be incorporated in the kinetic models (Taoukis and others 1997). The temperature dependence of the rate constant is most commonly expressed by the Arrhenius equation (Equation 20.3).

$$k = k_A \cdot e^{-(E_A/R \cdot T)} \tag{20.3}$$

where:

k_A = the Arrhenius factor (independent of temperature)

E_A = the activation energy (kJ/mol)

R = the universal gas constant (8.314 J/mol K) and

T = the absolute temperature (K).

An alternative to the Arrhenius law for expressing the temperature dependence of food deterioration is through the Q_{10} approach (Equation 20.4). The Q_{10} temperature coefficient describes the rate of change in a system (food, biological, chemical) as a consequence of increasing the temperature by 10 °C. Q_{10} is also defined as the ratio of the shelf-life at one temperature to that at a temperature 10 °C higher.

$$ln\ Q_{10} = 10 \cdot b = \frac{E_A}{R} \cdot \frac{10}{T+10} \tag{20.4}$$

where: b = the slope in the plot of the natural log of the shelf-life as a function of temperature.

Therefore by studying the deterioration process for at least two temperatures (higher than storage temperature) and applying the resulting data to the Arrhenius or Q_{10} equation, it is possible to predict the shelf-life of a given product at the desired temperature. This is actually an application of ASLT (Taub and Singh 1998; Galic and others 2009).

Mathematical models that incorporate the effect of a_w as an additional parameter can also be used for shelf-life predictions of moisture sensitive foods. Such models can also be developed based on the properties of the food and the packaging materials, and applied to packaged foods (Taoukis and others 1997).

The quality indexes that can be used for shelf-life estimation in bakery products are usually based on sensory and microbiological parameters in perishable and semi-perishable foods. In products with extended sustainability, chemical parameters, such as lipid oxidation, can also be considered. The points (tolerance or cut-off values) determining the end of a products' shelf-life are normally based on given standards, either legal or voluntary, but in their absence these have also to be determined based on experimental microbiological, chemical, sensory or physical (texture) criteria (Steele 2004; Taoukis and Giannakourou 2004; Guillet and Rodrigue 2010).

Another approach to shelf-life determination is through predicting the deteriorative changes resulting from different combinations of parameters. Predictive modeling (mainly for the prediction of microbiological behavior) or predictive equations, are based on statistical and mathematical relationships between the variables examined, resulting in the formulation of a suitable model. This model is subsequently validated to check the correlation between the experimental and predicted values and, if the degree of adjustment is satisfactory enough, the model can be applied in real food systems. Such models may reduce the need for shelf-life trials, but can only be used as a tool to assist decision making (Kilcast and Subramaniam 2000).

Several predictive equations have been formulated in the literature. Calligaris and others (2007) developed a shelf-life prediction model for lipid-containing bakery products taking

into account (i) the temperature dependence of the oxidation rate of bakery products, (ii) the acceptance limits indicated by sensory analysis, and (iii) the relationship between the chemical oxidation index and the acceptance limit. Their results highlighted that the peroxide value (linearly related to consumer acceptability) can be a representative index for the quality deterioration of biscuits during storage; and the evolution of peroxides can be predicted by a modified Arrhenius equation accounting for the changes in the physical state of biscuit fat (Calligaris and others 2007).

During storage, the textural behavior of bread products made from frozen dough can be predicted using simple equations, such as the second-degree polynomial equation. This was confirmed through experiments with different types of flour and storage periods, to establish the potential of the application of these findings to a variety of bakery products (Giannou and Tzia 2007).

Four categories of par-baked breads, namely variety, white, multigrain, and rye, stored under freezing conditions, were studied by Vulicevic and others (2004) to evaluate the effect of storage on product quality, and to develop prediction models (based on zero-order reaction kinetics) that describe the deterioration of selected quality parameters (sensory, chemical, and physical attributes and properties).

To estimate the sensory shelf-life of bakery products, based on the time necessary to reach a fixed percentage of consumers' rejection, survival analysis can be applied (Galic and others 2009). This methodology has been used by Gimenez and others (2007) to estimate the shelf-life of brown pan bread using the first significant difference in consumers' overall acceptability as the cut-off point. This point was calculated using the following Equation 20.5:

$$S = F - Z_a \cdot \sqrt{\frac{2 \cdot MSE}{n}}$$

(20.5)

where:

S = minimum tolerable acceptability of stored sample,

F = acceptability of fresh sample

Z_a = one-tailed co-ordinate of the normal curve for a significance level

MSE = 'mean square of the error' derived from the analysis of variance of the consumer data

n = number of consumers.

Survival analysis methodology was also used to estimate the shelf-life of Alfajor (a chocolate-coated individually wrapped cake). Sensory acceptability, off-flavor, and moisture content parameters (which were linearly related to time) were used to estimate the rejection level by consumers, and consequently shelf-life (Gambaro and others 2004).

Finally, challenge testing can be used for bakery products to validate their safety at a determined shelf-life and establish potential risks for the survival, growth, and/or production of toxins by specific foodborne pathogens. For this methodology, the food product under investigation is inoculated with a known pathogen, or non-pathogenic microorganism with similar characteristics, at a specific inoculation level and the survival and growth of the

inoculated microorganism are measured (Galic and others 2009).

Challenge testing was applied by Daifas and others (1999) to determine the safety of English-style crumpets (a high moisture bakery product), packaged under modified atmospheres. Samples were inoculated post-baking with *Clostridium botulinum* types A and proteolytic B spores, packaged either in air, in air with an oxygen absorber, or in a CO_2/N_2 (60 : 40) gas mixture and stored at ambient temperature.

Conclusions

The shelf-life of bakery products, representing the time during which they remain safe for consumption and retain their quality and nutritional characteristics at acceptable levels, can be affected by several intrinsic (raw material and formulation) and extrinsic (packaging and storage conditions) parameters. Among these, packaging is considered a key factor in delivering safe, wholesome, and attractive foods to customers. Several materials (such as flexible and thermoformed plastics), conditions (for example, MAP) or techniques (active or intelligent packaging) have been developed to cover all the different demands of the numerous bakery products available in developed countries.

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21
Process Optimization and Control

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Introduction

This chapter starts with the requirements of mixing dough so that the complex balance of chemical and physical changes that occur as flour and water convert to dough are understood. Mixing is of such importance to the baked goods sector that it has demanded a high proportion of research effort. It is often thought that the dough quality is optimal as the dough leaves the mixer and that subsequent processing stages can only serve to damage the gas cell structure. A section follows on dough development that describes some of the work done to optimize dough structure, which is followed by descriptions of the key mechanisms whereby oxidizing and reducing agents work in dough. The physical needs of developing an optimal dough structure are detailed in the section on different mixer types and in the section on alternative means of dough development such as sheeting. The final two sections focus on the heat and mass transfer operations of proofing, followed by baking and cooling. Less research work has been done in these areas although they are critical in ensuring that the quality of a baked product remains optimal.

Mixing

The process of mixing is a critical element of any bread making process as it is at this stage in which a number of critical processes occur. These include blending and hydration of the flour components, gas cell generation, and the start of the development of the gluten proteins. For no-time doughs, such as those typically produced in modern plant bakeries, the mixing element is wholly responsible for delivering dough with the appropriate structure and rheological properties for further processing. It is often stated that the dough is at its optimum immediately after mixing and that further processing can only serve to damage the delicate gas cell structure.

When flour and water are combined in a mixer, the first requirement is that components of the flour such as proteins and starches become hydrated. This is a prerequisite for subsequent operations because water is required as a medium within which molecules and enzymes become mobile and through which the many complex interactions that ultimately result in bread take place. This must commence relatively soon after the onset of mixing. What is less clear is the way in which the various flour components hydrate, the way in which this water is distributed and redistributed through mixing, and at what stage hydration gives way to the next process which, for the purposes of this description, is referred to as gluten development.

It is clear that gluten formation and development can occur only in the presence of water but it is less clear when this commences. The reason for this is that the initial part of the mixing curve (see Figure 21.1) shows an increase in resistance associated with the transition from dry flour and water to the viscoelastic dough. This increase in resistance continues over a period, up to a maximum value, and following this, resistance again decreases. Figure 21.1 was taken using a Farinograph, which is the standard instrument used by the bakery sector to determine the characteristics of a particular flour. This instrument mixes flour and water together while recording the torque. A flour sample of 50 or 300 g is mixed with a measured quantity of water to form dough. The amount of water determines the effective dough viscosity, or consistency, with less water increasing dough consistency, so moving the curve upward. A target torque of 500-Brabender units (BU) ± 20 BU is used (apart from in the United Kingdom where 600 BU is used for historical reasons) and the flour characteristics can be obtained by adding the appropriate amount of water and repeating the test.
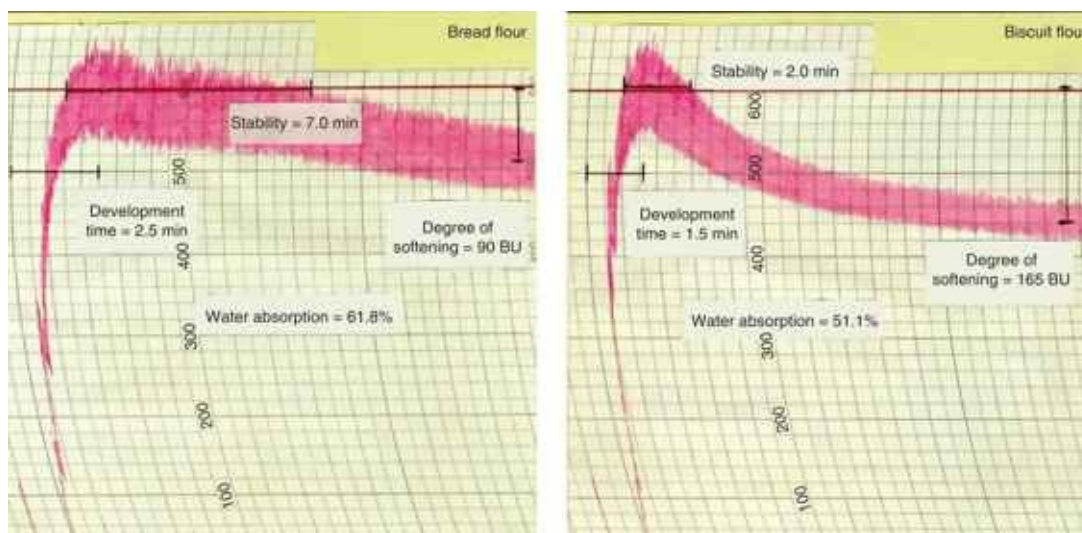
Figure 21.1 Typcal Farinograph curves for bread and biscuit flours. (Adapted from Bread Technology Course Notes, 2012).

Farinographs are given for two different flours: a high-quality flour for bread (Figure 21.1a) and a flour more suited to biscuits (Figure 21.1b). Several parameters can be obtained from the Farinograph but there are three key parameters used:

- Dough development time – the time required to achieve peak resistance.
- Dough stability – the time the dough retains it maximum consistency, which is the time difference between the curve first crossing the 500 line and when it departs the same line.
- Degree of softening – this is measured in BU and is the difference between the curve 5 min after it departs the 500 line. This can also be referred to as the mixing tolerance index (MTI).

Time to peak mixing is a fundamental property of individual flours, which is generally thought to relate to dough strength. Dough produced using strong flours generally requires a longer time to reach peak resistance. In this context, strong is related to the protein quality and is usually taken to be a description of the elasticity of the dough mixed. The more elastic the dough, the stronger it is generally perceived to be. It should be noted that while good elasticity is generally desirable for bread making, dough strength is not an absolute predictor of bread quality, but it is rather an indicator of the mixing regime required to optimize the quality of the bread to be produced. However, it is generally true that weak flours, which are unsuited to bread making, tend to have mixing curves where shorter times are required to attain maximum resistance.

As long as flour with good bread making potential is used, the dough tends to be at its most suitable for handling and bread making around the time at which resistance is at a maximum. Prior to this, the dough is considered to be underdeveloped, meaning the development of the gluten matrix is still ongoing. Beyond this point, the dough undergoes what is usually referred to as breakdown (Stauffer 1998) and becomes more extensible, less elastic, and stickier, making it more difficult to handle and with a noticeable loss in bread quality. The implications of this for optimizing dough development are the following:

- There is a point at which the dough quality and ultimately the bread quality will be optimized.

- Changes in dough rheology may be used as an indicator of when this point is reached.
- To control dough development effectively, a means of quantifying or indicating these changes is required.

Dough development

Wheat flour doughs are remarkably complex systems and although much research has been carried out, our understanding of the changes occurring during dough development is as yet incomplete. Nevertheless, there are a number of areas of scientific work that allow an understanding of the molecular basis of dough development. It is important to recognize that although this discussion will primarily focus on wheat flour proteins, there are several other factors that, while not covered here, are nonetheless important. These include, but are not limited to:

- the level of damaged starch produced during milling;
- the concentration of water-soluble and non water-soluble arabinoxylans from the cell wall material;
- the physical characteristics of the starch granules;
- the milling extraction rate;
- other functional materials added to the mixer.

Nevertheless, it is generally accepted that the key component in the unique ability of wheat to form viscoelastic dough are the wheat proteins, specifically those fractions which form gluten when hydrated. Wheat proteins comprise at least 70 different proteins (Belton 2002), but to assess their functionality they may be classified into four main groups according to their solubility in various liquid media (Osborne, 1907). These groups are detailed in Table 21.1. While all of these fractions are important to the wheat plant, either as metabolic (the albumins and globulins) or storage (gliadins and glutenins) proteins, it is these latter groups that form gluten on hydration and in doing so confer the viscoelastic properties of a wheat flour dough.

Table 21.1 Osborne fractions of plants generally and wheat proteins specifically

Solubility	Plant protein fraction	Wheat protein fraction
Water soluble	Albumins	Albumins
Saline soluble	Globulins	Globulins
Aqueous alcohol soluble	Prolamins	Gliadins
Remaining insoluble fraction	Glutelins	Glutenins

Gliadins are made up of monomers and are thought to confer extensibility to dough while the glutenins form the polymeric fraction and confer elasticity. Both high-molecular-weight and low-molecular-weight glutenins exist, with the former being the better characterized and more directly associated with dough properties in the work to date, as discussed elsewhere.

Optimization of the mixing process requires an understanding of the way that gluten forms in the mixer. Early workers recognized the importance of the cysteine residues contained in the

glutenin fraction. It was reasoned that the structure of gluten had to be extensively cross-linked to produce the resistance to extension typical of wheat flour doughs, and the formation of disulfide bonds between and across individual glutenin units was proposed as the means by which this occurred (Schofield 1986). The cross-linking in the gluten matrix is illustrated in Figure 21.2. These disulfide bonds were thought to emanate from the thiol groups present on the cysteine residues in gluten proteins. Evidence for this was supplied by the fact that oxygen was shown to be a key requirement for dough development. This is demonstrated by mixing studies in which dough was under-oxidized (Baker and Mize 1941).
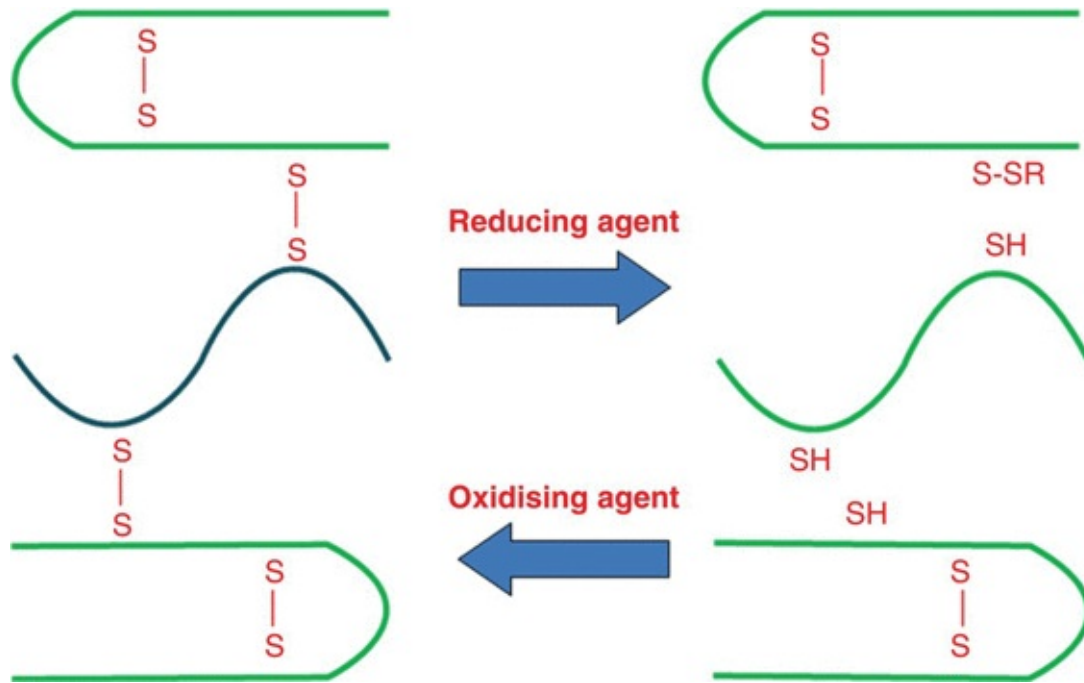
Figure 21.2 Cross-linking of the gluten matrix. (Adapted from Bread Technology Course Notes, 2012).

In addition to this work, the action of oxidative improvers such as dehydro-ascorbic acid (the active improver formed when ascorbic acid is exposed to oxygen under aqueous conditions), potassium bromate or azodicarbonamide also indicates that oxidative conditions are required during mixing for optimal dough development to occur (Cauvain and Collins 1994).

Although the importance of the formation of disulfide bonds in dough structure is widely accepted, recently authors have highlighted the importance of other systems that seem to contribute to the doughs' characteristic rheology. The first of these, hydrogen bonding, has long been recognized as a factor due to the changes in dough rheology observed when D_2O is substituted for H_2O (Tkachuk and Hlynka 1968). More recently, however, spectroscopic techniques have led to the development of the so-called loop and train model (Belton 1999) in which it is postulated that individual glutenin subunits interact with one another by disulfide bonds at the ends of the subunits and hydrogen bonds along the repeat region. The interaction between the repeat regions of adjacent subunits leads to zones of trains where the molecules are closely associated and loops where water is bound to one or both of the subunits. Extension of the system pulls the loops straight such that the loops disappear and trains are formed. Relaxation of the system allows the loop regions to reappear.

Another theory about the changes occurring during mixing (Hoseney 1986) proposed that the increase in resistance up to the peak was due simply to hydration of the flour proteins. As they gradually become hydrated, the amount of mobile water decreased up to the point at

which the proteins were fully hydrated (the peak). Following this point, irreversible changes in the gluten polymers occurred.

Oxidising and reducing agents

It has been stated above that the chemical changes in S–S (disulfide) and S–H (thiol) bonds that occur during dough development can be induced by using oxidizing and reducing agents. Oxidizing agents are used to enhance creation of the disulfide bonds that strengthen the gluten matrix, whereas reducing agents do the opposite and make the dough flow more easily. The principle bonds involved in dough rheology are the thiol and disulfide bonds, in addition to the weaker but more numerous hydrogen bonds.

One of the most commonly used oxidizing agents is now ascorbic acid, otherwise known as vitamin C. Interestingly, ascorbic acid is an antioxidant, which means that its natural function is as a reducing agent. It must first react with oxygen to form the intermediate compound dehydroascorbic acid, and it is this that acts in the oxidizing function. The conversion of ascorbic acid to dehydroascorbic acid is catalyzed by the ascorbic oxidase enzyme that is found naturally in flour. This reaction is temperature dependent, as are all enzyme-catalyzed reactions, and is favored by warm dough temperatures of say 25–35 °C. Oxygen to encourage formation of this intermediate compound is obtained during the dough mixing and therefore an optimized mixing process must provide sufficient oxygen for this reaction to take place.

However, it is possible to over dose with ascorbic acid so that it behaves in its natural reducing agent form. Levels of addition need to be of the order of 200 mg per kg flour (Xiuzhen and Seib 1998). This compares with typical addition levels in plant bakeries of 40–100 mg/kg. Ascorbic acid levels can be reduced if additional oxidizing agents such as azodicarbonamide (if permitted) or oxidase enzymes are added in combination.

Oxidizing agents are usually required for generating the fine gas cell network in dough during mixing; however, there are some bread products that require the dough to flow. Examples are pizza bases, hamburger buns, and some pan bread. In these cases, the requirement is to break the disulfide bonds using reducing agents such as l-cysteine, protease enzymes or sodium metabisulfite (if permitted). Cysteine, for example, converts the disulfide bonds between adjacent gluten molecules to thiol bonds. This weakens the gluten matrix by breaking the bonds between adjacent gluten molecules that are then free to move relative to each other. The effect is a reduction in dough viscosity as well as reduced elasticity. This latter feature is important in hard dough biscuits where shrinkage of the molded biscuit is undesirable and can lead to an oval biscuit shape. Shrinkage of croissant dough is another application in which cysteine or a protease enzyme is usually added to the dough to reduce the elasticity of the dough and prevent the recoil in shape.

The effects of mixer type

In addition to differences in the mixing action that results from blade and bowl design, a key distinction between mixers is the intensity of their mixing action, that is how quickly the mixer `works' the dough. In order to develop dough during mixing, as carried out commercially, it is important to understand differences between the mixer types used. In terms of intensity, mixers can be thought of as falling into one of four broad groups: low,

medium, high, and very high.

Low-intensity mixers include traditional systems such as the Artofex mixer, as used for dough that will undergo bulk fermentation. The Artofex mixer (Figure 21.3) was designed to replicate the hand and arm movements of a craft baker. Dough is worked in a very gentle fashion, giving a similar effect to mixing by hand, and as with hand mixing, the mixing times are very long (typically ~ 30 min). One advantage of this is the large margin of error on mixing time that make optimization a simple process. Optimal mixing times are less critical for subsequent processing than other factors such as the dough temperature or fermentation time. In fact, the mixing intensity is so low that over-mixing of the dough is not thought to be an issue. However, it is unlikely that low shear mixing regimes can produce high-quality dough in the absence of subsequent dough maturation by lengthy fermentation.

Figure 21.3 Artofex mixer developed to replicate hand and arm movement of bakers.

Medium-intensity mixers include spiral type mixers that are probably the most common mixer type for baked products globally (Figure 21.4). Their energy input for a given mixing time at high speed is relatively high when compared with an Artofex mixer. However, the optimal mixing times in the dough development phase (rather than the slow speed incorporation phase) are about 8–12 min. Typical high speeds are about 150–250 rpm, which tends to cause a temperature increase in the dough of 6–7 °C. Although these mixers may be used for processes where bulk fermentation or sponge systems are used (that is, where other mechanisms contribute to dough development), they may also be used in no-time dough systems where fermentation is limited to proof of molded pieces immediately prior to baking. This indicates, therefore, that the levels of gluten development can be sufficient to produce dough in the absence of long fermentation steps. Optimization of mixing concerns the use of the correct high-speed mixing time for gluten development. Manufacturing tolerances in the spiral design are known to cause differences in the mixer performance, and it cannot be assumed that two spiral mixers of the same design will mix the same.

Figure 21.4 Medium intensity mixer of the spiral design.

High-intensity mixers include the horizontal bar mixing systems that tend to be popular in North America (Figure 21.5). Here, mixing times are shorter than with spiral mixers, typically 6–8 min on high speed. The maximum speed of a bar mixer would be about 150 rpm, slightly lower than with a spiral mixer. This is because the rotating bars create considerably more shear than with spiral mixers, which allows for shorter mixing times. The result is faster dough development and a greater dough temperature rise. Gluten development is often achieved using sponge and dough processes in combination with mixing action.

Figure 21.5 High intensity mixer of the horizontal bar type.

Very high-intensity mixers tend to be used in speciality processes such as the Chorleywood Bread Process (CBP). In this case, mixers are used as the sole mechanism for developing the gluten structure and initiating gas cells in no-time dough. The ability of high mixer speeds to produce rapid gluten development was first noted by Swanson and Working (1926). The first commercial application of this was the Do-Maker system from the 1950s, although it was the CBP development that combined all the elements required to allow high-quality bread to be produced from much shorter processes (Chamberlain and others 1961). Since then, the generic term mechanical dough development (MDD) has been adopted to cover similar processes. Typical impeller speeds are about 350–500 rpm, which tends to cause a temperature increase in the dough of around 15 °C.

A key element of the CBP is the delivery of a fixed amount of work to the dough in a short period. In the case of CBP, this was stipulated to be 39.6 kJ kg^{-1} (11 Wh kg^{-1}) within 2–5 min,

and this figure is still used by many bakeries in the United Kingdom where the process was developed. It is important to note, however, that the optimum level of work varies with flour of different quality protein (Cauvain and Collins 1994; Gould 1998). Optimization of mixing requires the flour protein quality to be matched to mixing work input. It is generally recognized that increasing the flour protein quality demands a higher work input because there is more gluten that must be developed. Within the United Kingdom the range of energy input varies from as low as 10 Wh kg^{-1} up to around 13 Wh .kg^{-1}.

Another way to optimize the dough development during mixing is to control the atmosphere above the dough. The effect of a partial vacuum applied towards the end of mixing in Tweedy type mixers (see Figure 21.6) promotes a fine and uniform crumb texture. The development of an over-pressure stage at the beginning of mixing was introduced as recently as the 1990s, however, to ensure that significant oxygen was available to the dough during the early stages of mixing. This promoted faster gluten development and thus ensured that the action of oxidizing improvers was maximized (Collins 1993). Pressure and vacuum are applied for approximately equal times to achieve the optimum gas cell structure in bread.

Figure 21.6 Very high-intensity mixer of the Tweedy type, used for the Chorleywood Bread Process.

Process

As stated earlier, in 1961, the British Baking Industries Research Association (BBIRA) developed a no-time dough process that was controlled by the energy input to the dough (CBP). The CBP uses high-shear mixing to achieve physical changes in the dough that were traditionally brought about over extended time periods by fermentation. These desirable changes required the presence of a small amount of added fat and an oxidizing agent, now usually ascorbic acid. There are subsequent processing stages following mixing which include a dough relaxation period followed by cutting each molded dough piece into four and turning

each piece through 90° when placed in the pan. This is an example of a further process optimization step that has produced bread with a fine, even structure and white crumb appearance.

Alternative dough development method – sheeting and lamination

The earlier descriptions include various types of dough mixer in which a mixer blade of some design rotates within a mixer bowl, and in doing so imparts a cutting and/or shearing action on the dough. This firstly hydrates the dry components and secondly developes the gluten matrix, which is essential for the structure of bread. However, not all bakeries develop their dough by mixing alone. In Central and South America, Africa, and parts of Asia, sheeting processes similar to those used for pastry are used (Bushuk and Hulse 1974). The number of sheeting passes can be thought of as similar to the time of mixing, in that the dough changes its rheological properties and the gluten matrix develops with increased shear. As with mixing, an optimum exists and excessive sheeting can result in breakage of the disulfide and hydrogen bonds between gluten molecules and the gas holding quality of the dough is reduced.

One advantage of sheeting is its lower energy requirement compared with mixing. It is reported that sheeting only requires some 10–15% of the energy associated with other mixing types (Kilborn and Tipples, 1972a, 1972b); however, the data are for pilot systems and the scale up to commercial bakery systems is less certain. Also, the studies are unclear how much energy is taken into account for the essential 'premixing' stage in which the dry and wet ingredients are combined to make an under-developed dough prior to sheeting. Nevertheless there is widespread agreement that sheeting is less energy intensive than mixing (Levine, 1998; Sutton and others 2003).

As well as the energy claims, one further benefit of sheeting is the improvement in bread structure that can be achieved. This benefit is being realized through an ongoing patented process that uses dough sheeting followed by dough cutting that encourages the bubbles to align in one direction (Campden Technology Limited 2010). This is known as the Radical Bread Process (RBP) and is being developed by Rondo (Switzerland). The RBP comprises a number of sequential steps, which include the following:

- combining the ingredients into an underdeveloped dough;
- subjecting the dough to deformation shear by using sheeting;
- cutting the developed dough into pieces;
- positioning the dough pieces in a pan so the laminations lie in one direction;
- proofing, baking and cooling as for pan bread.

Underdeveloped dough can be produced in any mixing system by combining the ingredients in the mixer just long enough for the water to absorb into the flour so the dough can be moved to the sheeting stage. Temperature rise in the dough is minimal because of the low energy input.

The two key steps that provide the unique bread structure shown in <u>Figure 21.7</u> are (a) sheeting to create layers and (b) cutting the dough so the layers align in one direction. This

yields dough in which most gas cells are disk-shaped ellipsoids. Dough pieces are placed together in a pan, each piece being oriented in such a way that the polar axis of the ellipsoid gas cells coincides with the length dimension of the pan. During the subsequent leavening by yeast, the gas cells become elongated in a vertical direction. The bread loaf obtained by baking this dough exhibits a unique cellular structure, which was found to increase resistance of the bread crumb against tear during the application of spread. Furthermore, slices of the loaves have a very bright appearance because of the shallow gas cells and a regular shape that makes them ideal for the industrial production of sandwiches. Some key texture and C-Cell parameters that are used to define bread quality are presented in Table 21.2.
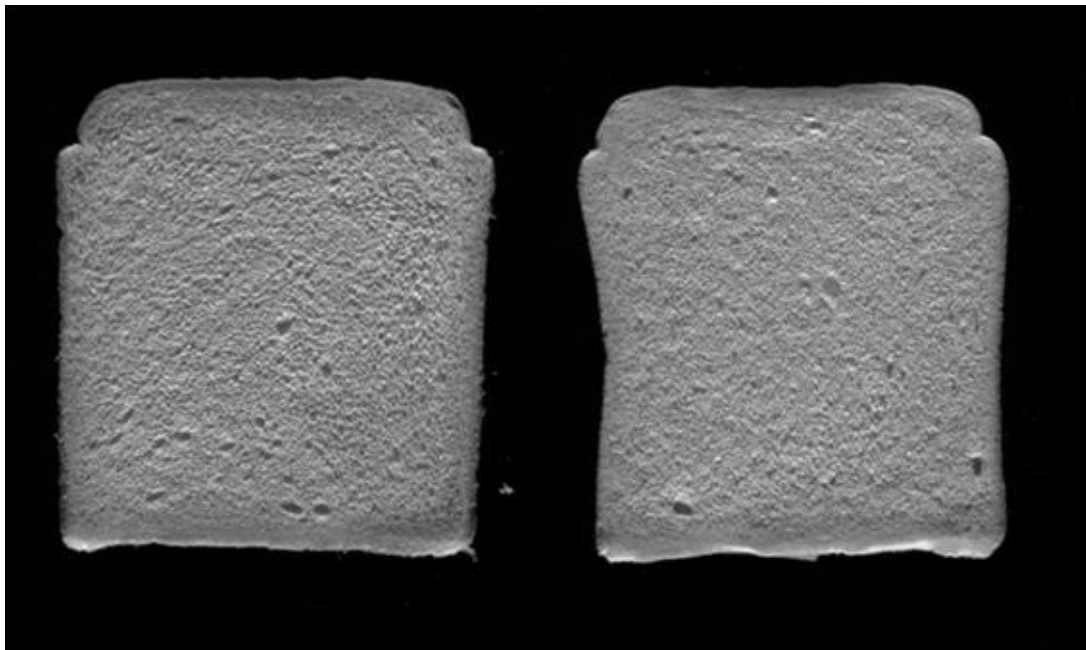
Figure 21.7 CBP loaf structure (left) and Radical loaf (right) as assessed by C-Cell.

Table 21.2 Texture and C-Cell parameters show key differences between slices of white bread made by the RBP and CBP. Data are average slice values throughout the loaf

	Radical Bread Process	CBP
C-Cell™ number of cells	12 680 ± 465	11 402 ± 310
C-Cell™ cell volume	3.30 ± 0.12	4.02 ± 0.09
C-Cell™ cell contrast	0.8232 ± 0.008	0.7895 ± 0.005
Firmness (g)	116 ± 18	153 ± 24
Specific volume (ml/g)	4.36 ± 0.08	4.21 ± 0.07

Optimizing dough development

It is clear from the preceding sections that there are major chemical and rheological changes that take place in dough during mixing. Optimization and control of mixing in plant bakeries, however, commonly relies on measurements such as:

- mixing on high speed for a fixed time;
- mixing to a fixed energy input;
- mixing to a fixed dough temperature or, more correctly, temperature rise;

- mixing to a fixed dough consistency.

Of these, the first two are probably in widest use although the others have been applied.

Mixing to a fixed time is applied in processes for spiral and bar mixers. It is effective because the longer mixing times allow a greater margin for error such that differences in flour quality do not result in the need for greatly different mixing times. Where higher-intensity mixers are used, such as the Tweedy (Baker Perkins, UK), mixing to a fixed time becomes impractical because the margin for error becomes less in absolute terms. For example, a 1 min difference in mixing time has a proportionately greater effect when the total mixing time is 3 min rather than 10 min.

Mixing to a fixed energy input is more common for higher intensity mixers. Although high-intensity, no-time dough processes such as the CBP tend to rely on a fixed work input as a means of controlling dough mixing, the time over which this work input must be delivered has always been stipulated (Chamberlain and others 1967). Optimum results were achieved in the original development work for a fixed work input of 39.6 kJ kg^{-1} (11 Wh kg^{-1}) when this work was delivered within 2–4 min (although an upper limit of 5 min was accepted as the absolute limit for production of bread of acceptable quality). This study also demonstrated that bread quality was affected by not only total work input but also the rate at which it was carried out. In fact, the variation in mixer rate was found to be most marked for strong flours, with higher rates of mixing for strong flours of Canadian origin being a means of adjusting for situations where a reduced total level of work input was delivered.

Mixing to a fixed dough temperature, or temperature rise, is a method that is not often used commercially. The rise in dough temperature during mixing is a natural consequence of the work expended in shearing and deforming the dough within the mixing chamber. This method requires control of the ingredients' temperature as well as consistency in the energy lost from the mixer. In bread dough mixing, the final dough temperature should ideally be controlled because it has a direct effect both on how the remaining parts of bread making (such as proof) proceed, as well as how the dough will pass through the molding equipment. Where high energy levels are used to develop the dough, the mixing bowl must be cooled to ensure that the large temperature rise associated with high-intensity mixing does not produce a dough at the end of mixing that will be difficult to pass through the plant or that will proof too quickly.

During the 1960s and 1970s, much work was carried out at the former Flour Milling and Baking Research Association (FMBRA) investigating the processes associated with the production of semi-sweet biscuits or cookies (Wade and others 1965). For these products, some gluten development is desirable to ensure that the dough withstands sheeting, but over-tough or elastic gluten properties should be avoided to ensure that the cut dough does not pull back to an oval shape after cutting. This work showed that while the work input during mixing was an important aspect of ensuring that the required changes took place, mixing to a final temperature in the range 37.8–43.3 °C was also important to deliver optimum dough quality for subsequent processing. This was to some extent dictated by other changes that were temperature related, for example the solubilization of the sucrose in these recipes.

Nevertheless, this work is relevant to the study of bread dough mixing as it shows, first of all, the potential of the use of temperature rise as a control mechanism. Secondly, it also

demonstrates that temperature rise has many consequences for the underlying chemistry of the system. Most scientists and technologists will be aware of the increased rate of many reactions at higher temperatures and the changes in rheology that occur for materials when their temperature is changed. This should serve to alert us to the possibility that the increased temperature of the dough itself is an important factor in the process of working the dough as well as the energy that is required to raise the temperature.

One additional complexity when mixing to a fixed dough temperature or temperature rise is how to measure the temperature within a large mass of dough. Temperature sensors within the mixer bowl can only penetrate a few millimeters into the dough, otherwise the high shearing conditions could damage the probes. A short temperature probe may not measure the correct dough temperature because the dough nearest to the periphery will be more affected by the bowl jacket temperature than dough within the bulk.

Mixing to a fixed dough consistency is rarely used to control mixing. This is surprising given that the basis for many decisions on the mixing parameters is derived from Farinograph curves, which use torque measurements. One of the key skills required of bakers has always been an ability to judge the consistency of dough by manual manipulation, and adjust the process accordingly. Torque measurement is now relatively inexpensive to implement and is a non-invasive technology. Another argument in favor of dough consistency control is that mixing to fixed energy input can result in control where the flour properties change little, but it clearly cannot achieve the same level of dough development where the flour properties are very different.

Proofing

Proofing is one of the most time-consuming process steps during the entire baking process but is given less technical attention than mixing. The objective in proofing a no-time dough is to generate carbon dioxide from yeast activity and in doing so increase the dough volume. Typically 90% of the bread volume is achieved in the proofer with a further 10% from the oven spring. There are two basic requirements of the proofing operation, which are to operate at dough temperatures in which the yeast is very active and to use high humidity levels so a skin does not develop on the dough. Hence proofers are usually set at 38–43 ℃ and 70–80% humidity.

What is often ignored is that a proofer is not designed to be a heat transfer device. Compare this with a convection oven that uses fans to circulate air to create surface turbulence and in doing so transfer heat effectively from the environment to the product surface. Proofers do not tend to have circulation fans and must rely instead on high humidity that will undoubtedly help to increase the surface heat transfer coefficient but not to the extent of a fan. Hence, cold dough will take a long time to increase in temperature during proofing, making the proofing process a bottleneck.

Optimizing proofing can only be effective if the dough gas cell structure and dough temperature are also optimized during mixing. Hence it is essential to understand the interactions between mixing, proofing, and baking. Effective process optimization can only be achieved if each of these processes are analyzed together (Hall 2003). During mixing it is necessary to create a network of small gas cells in the dough so the yeast cells can utilize oxygen from the cells and inflate each of the bubbles. This requires the optimal use of minor ingredients such as enzymes, emulsifiers, and oxidizing agents. A detailed analysis of the use of these minor ingredients is beyond the scope of this chapter but can be found in Part 3 of this book. If the dough mixing is suboptimal it is unlikely that subsequent process steps will be effective.

One of the most important parameters in optimizing mixing is to achieve a dough temperature at the end of mixing that allows the dough to expand effectively while retaining as many of the individual gas cells as possible. Dough has an aerated structure that is an effective insulator. A consistent dough piece temperature during proofing will result in greater uniformity of the inflated gas cells throughout the dough piece. This will generate uniformly sized gas cells and a desirable appearance of the baked bread. Dough that enters the proofer too cold, for example below 28 ℃, will not have sufficient residence time in the proofer for heat to penetrate through to the dough piece centre. Yeast action will be fastest towards the outside of the dough pieces with the result that gas cells will remain smaller towards the centre. During baking this can result in non-uniformity in structure across a slice taken from the baked loaf. Compression layers near to the crust are typical of uneven proofing, as shown in Figure 21.8.
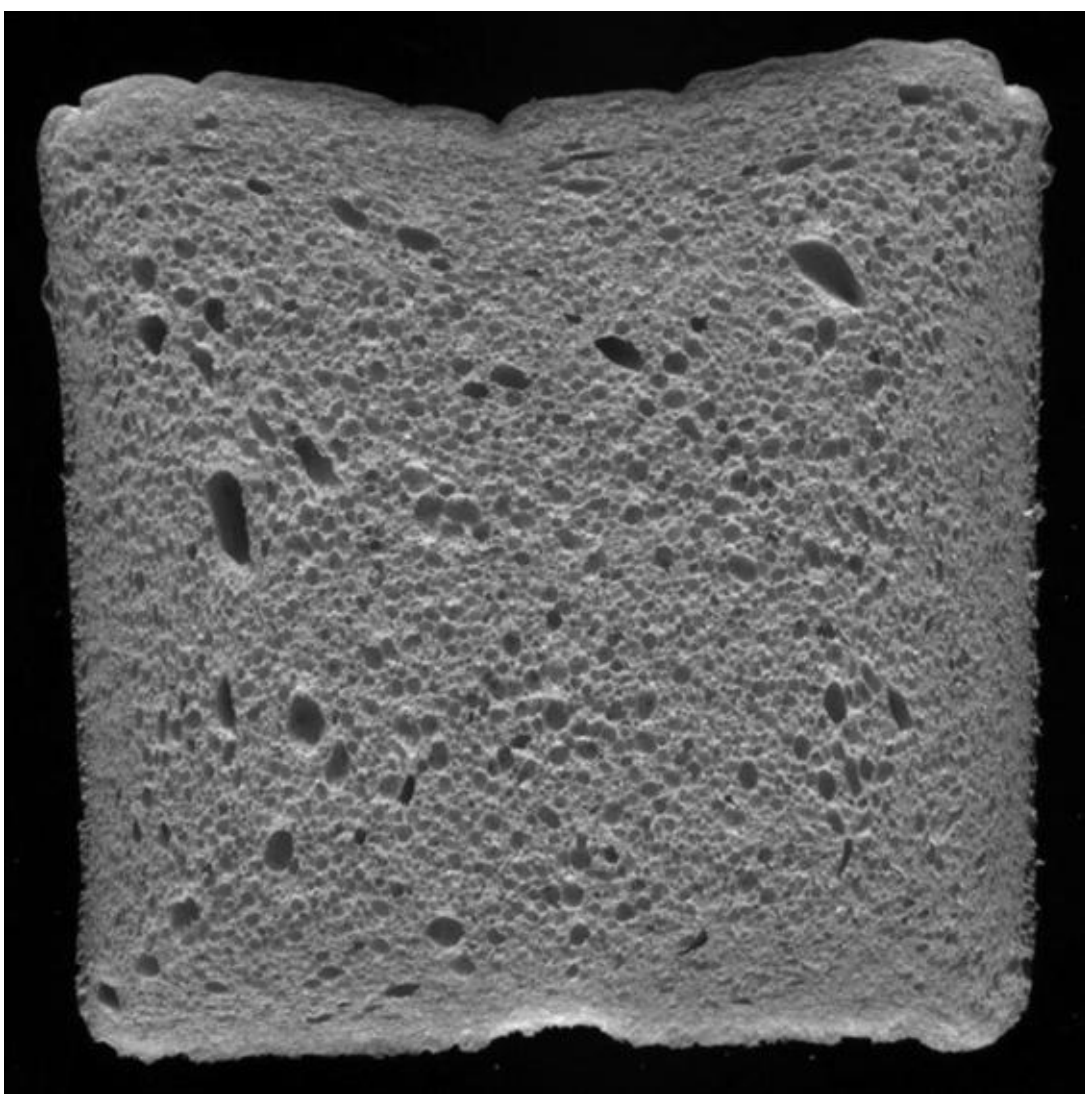
Figure 21.8 Slice taken from an 800 g lidded white loaf showing compression layers near the crust.

When considering an optimization study of proofing it is therefore important to include the mixing process in the study. Dough temperature change between mixing and proofing should be minimized. Dough temperature at the end of mixing should be as high as can be handled in the bakery before the dough becomes too soft and sticky. As a general rule a dough temperature of 28–30 °C is considered to be as warm as most plant bakeries can work with.

Baker's yeast works optimally at 34–36 °C and so the proofer should be set close to this temperature range. Most bread proofers are set at 38–42 °C because of the need for higher temperatures than the dough to gain benefit from a temperature driving force that maximizes heat transfer into the dough and keeps the proofing time short. It is debatable whether this is good practice and the emphasis should instead be placed on achieving a higher dough temperature. This will speed up the proofing process because the dough is already close to the optimal yeast temperature with the result that the proofer temperature can be set closer to 38 °C than 42 °C. A lower proofer temperature, closer to that of the ingoing dough, will result in more uniformity in gas cell expansion throughout the dough pieces.

The humidity level possibly has a greater influence on heat transfer than the proofer temperature. It is always good practice to operate with humidity at its highest level for the dough. This prevents skinning of the dough pieces. If a dough piece forms a dry skin this will prevent its expansion and the result can be smaller bread during baking. There will also be

more surface cracking that will give rise to an undesirable appearance. Bread dough typically has a natural relative humidity above 95% and therefore during proofing at 70–80% humidity, the dough pieces will lose a small amount of water to the environment, about 3 g in an 880 g dough piece (Wiggins 1998).

The discussion on proofing has considered the ideal conditions of proofer temperature and humidity to suit the needs of the dough. With energy prices going ever higher, it is also important to consider the costs of energy used in proofing. Processing with the highest dough temperature that can be handled in the bakery will help reduce the heat that must be transferred in the proofer. Further energy saving should consider the location of the air intakes to the proofer as well as rates of leakage from the proofer. Most proofers will draw ambient air directly from the bakery. A more energy effective way is to position the proofer directly above the oven so that the heat from the oven is used to maintain the proofer temperature. Several recent installations of ovens and proofers have adopted this principle.

Baking and cooling

Baking is the most energy intensive process step in the manufacture of baked goods (Carbon Trust 2011). With increasing pressure on reducing energy and carbon footprint, it is prudent that the baking process should be the focus for optimization measures. Bakery ovens can be either directly fired by gas burners or indirectly heated by gas or electricity. Radiation, convection, and conduction are all used in bakery ovens, with any one type of oven using at least two of these heating modes. Typical oven temperatures for bread are between 200 and 270 °C with baking times of 20–25 min for 800 g loaves. For cakes the range of temperatures and times is greater because of the size differences with products and the high levels of sugar that can generate browning at faster rates than with bread. Oven temperatures as low as 150 °C are common for large cakes but will require baking times of 2–3 h. For biscuits it is usual to set ovens at 250–300 °C and bake for 5–10 min.

Optimization of baking is about reducing the energy used during the baking process without compromising the baked product quality. The temperature change measured at the core of a biscuit during baking is shown in Figure 21.9. There are three distinct stages of biscuit baking that help with optimizing the baking process: structure development, drying, and color formation. Each has its own requirements for the oven conditions.
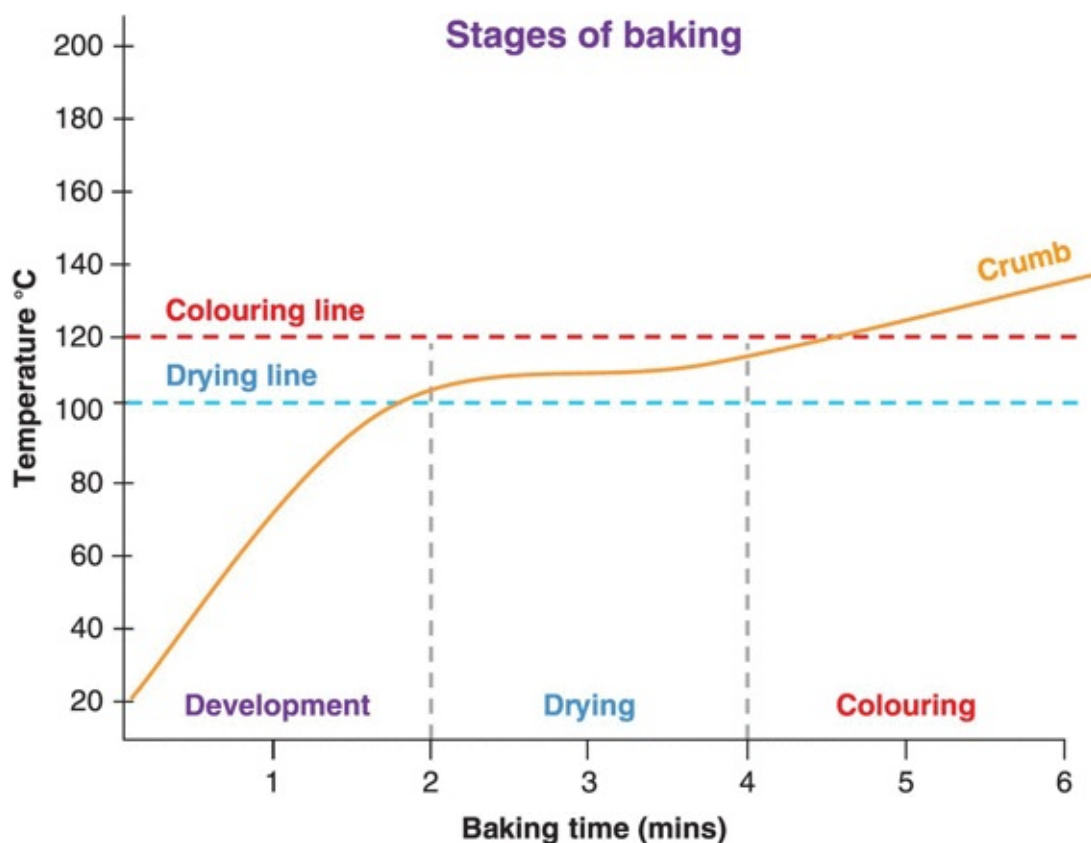
Figure 21.9 Core temperature rise during biscuit baking showing the three oven stages. (Adapted from Bread Technology Course Notes, 2012).

The three stages of baking are relevant to most types of baked product; however, the description of each stage given here is for a biscuit dough. Analysis of the ideal oven profile that meets the needs of each stage can be evaluated for bread, cakes, pastry, and speciality baked products. By undertaking this evaluation, it is possible to optimize the baked product structure.

Development stage. During this stage the dough changes from its raw dense state into an aerated structure in which the proteins and starches have started their chemical and physical transformations. Raising agents will release carbon dioxide, which, together with gases released from solution, thermal expansion and steam, will create lift in the biscuit dough. High humidity is best suited to this stage so that the surface remains soft and can accommodate the rise without cracking. Ovens with dampers are usually operated with the dampers fully shut during the development stage. This allows a build-up in humidity caused by water vapor from the biscuit dough and from the combustion products, if a direct fired oven.

Drying stage. Dough temperature will reach 100 °C at the start of this stage. Water is driven off at a rapid rate and it is important that the oven can remove the water vapor from the biscuit surface. This allows more water to be evaporated and so keeps the drying rate high. Much of the biscuit volume increase has already been achieved in the development stage and the surface can now be dried without risk of expansion cracks. High oven temperature, fully open dampers, and high rates of air turbulence are all ideal to remove water.

Color formation stage. There are two main color reactions that give rise to the desirable brown crust and paler crumb color. Maillard browning takes place above approximately 105 °C and requires the presence of a reducing sugar (glucose, maltose or lactose) together with an amino acid, the type of which determines the color and flavor. The second color reaction is caramelization of the sugars at 160 °C and higher. Color changes are from yellow through brown and finally black. A lower oven temperature (than with the drying stage) is desirable to control the biscuit surface temperature so it does not end up with a blackened surface.

Selecting the optimal product core temperature as it exits the oven is important to avoid under or over baking. For example, baking of bread has traditionally used an end of baking core temperature of 94–96 °C as the target. This temperature is based on both microbiological and structural criteria albeit with an operational margin.

- The microbiological needs are to remove vegetative cells that could grow in the bread during its ambient shelf-life. Bacterial spores will be relatively unaffected by the bake and rely on the presence of other preservation hurdles to prevent their outgrowth such as propionic acid. Achieving 94–96 °C is not a critical control point (CCP) for the process because it does not correlate with the microbiological safety target of 70 °C for 2 min for a 6-log kill of *Salmonella, Listeria,* and *E. coli* (Tucker and Featherstone 2011).

- The structural need is to achieve fully gelatinized starch in the crumb so that the internal structure sets during cooling and remains in this condition during shelf-life. It is the starches rather than the proteins that are most important for the baked product structure. Wheat starches gelatinize between 60 and 80 °C if no sugar is present, but this temperature increases as the sugar content increases.

Indications are that 94–96 °C for bread is higher than necessary for either the microbiological or the structural needs; however, it has rarely been challenged. A lower core temperature after baking will correlate with less water being evaporated and so the baked loaf will have higher moisture content than its control unless the recipe or scaling weights are adjusted. Research on optimization of energy use during bread baking is ongoing at Campden BRI by challenging 94–96 °C and making changes to the mixing, proofing, and baking process as a means to save energy at each stage. This is not an easy task because of the interactions

between stages of the bread making process such as mixing, proofing, and baking.

The rise in temperature at the surface and core of an 800 g lidded loaf are illustrate in Figure 21.10 and Figure 21.11, respectively. Key events are marked, for example, the temperatures at which the color changes first take place are given in Figure 21.10, and the sequential changes that result in oven-spring are given in Figure 21.11. As a result of this, optimizing the baking process must take into account all of the physical and chemical changes. It is very difficult to change one factor without affecting another. For example, increasing the yeast level as a means of reducing proofing time can have an effect on the surface color because of changes to the available sugars.
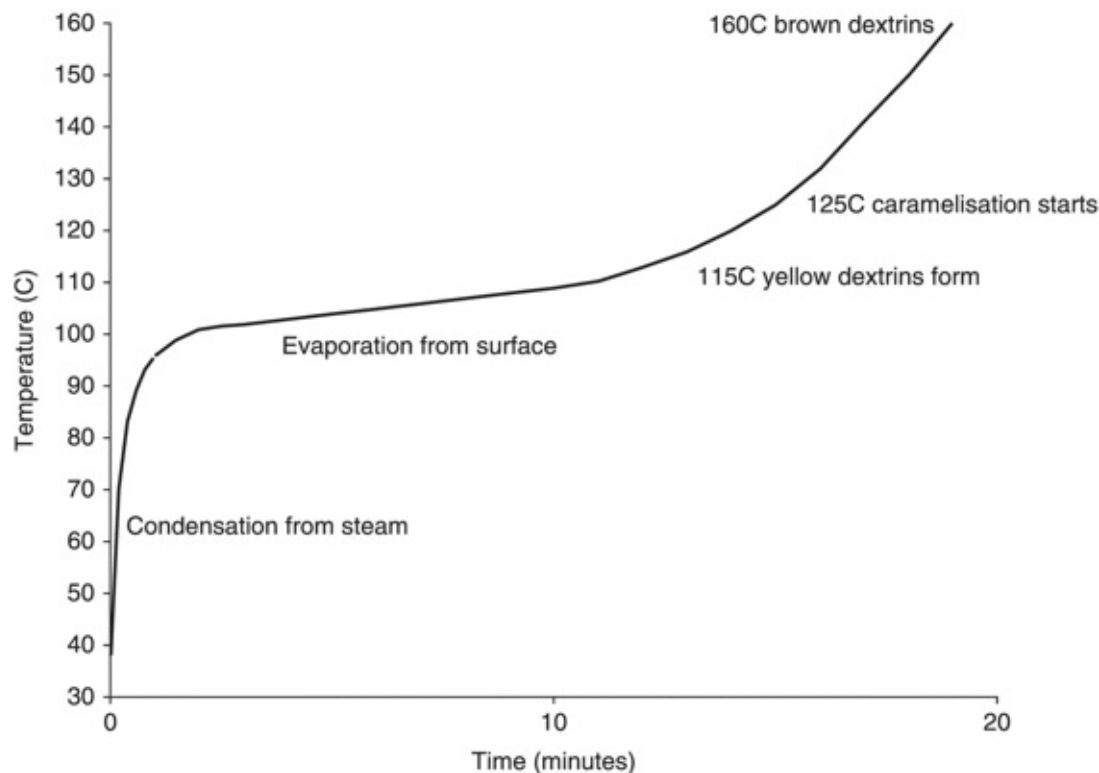
Figure 21.10 Surface temperature rise during bread baking in an oven at 240 °C, showing some key events. (Adapted from Bread Technology Course Notes, 2012).
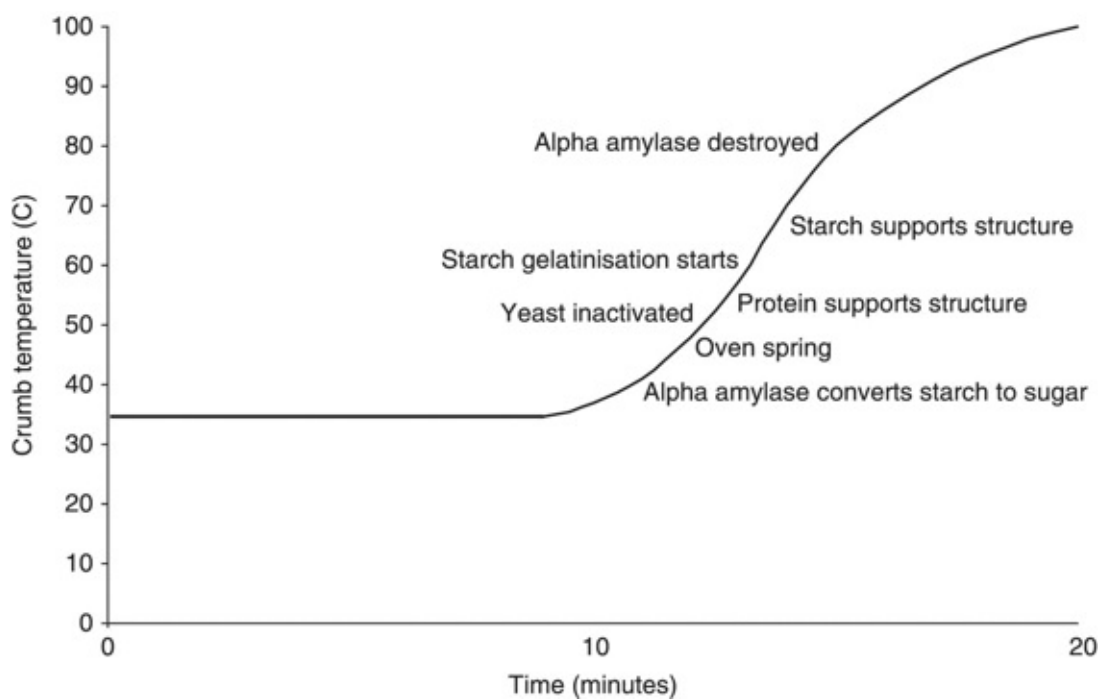
Figure 21.11 Core temperature rise during bread baking in an oven at 240 °C, showing some key events.

The mechanism of heat transfer within a bread product differs markedly from other food products. For example, a comparable size meat product would require two to three times as long to reach 94–96 °C at the core. This is partly because of the lower specific heat capacity of bread and bread dough when compared with meat, but more importantly it is caused by the unique evaporation–condensation mechanism found in bread. Gas cells in bread dough create chambers in which steam is generated at the hot side, which moves rapidly to the cold side where it condenses. This gives rise to a very high heat transfer rate through the dough. This mechanism does not happen with most other food materials because of the lack of intact gas cells. It does, however, take place to a lesser extent in cake but the elastic gluten network is less developed than with bread and so there is some leakage of steam from the cells. This reduces the heat transfer rate.

The evaporation–condensation mechanism in bread is so effective that increasing the heating rate further from surface to core will not provide much commercial benefit. Instead, it is better to invest effort into optimizing the time during proofing and cooling as this should result in cost savings. For example, proofing of an 800 g loaf takes approximately double the time during baking, and the cooling process takes about six to eight times as long. Both processes involve considerable quantities of dough and bread being held up in large chambers. In addition to the product value held up in the proofer and cooler, this causes the bakery major problems of product losses when line stoppages occur. Reducing proofing and cooling times can therefore help reduce these losses.

Typical cooling times for 800 g loaves of bread are around 90–120 min if ambient air is used. Cooling times can be reduced by increasing the temperature driving force through the use of refrigerated air towards the end of the cooling process, typically taking cooling times down to 60–90 min. A reduction can also be made using saturated air because of the increase in cooling rate that can be achieved with increased humidity. This also has the advantage that water loss is reduced, leading to higher bread weight or more importantly the possibility to reduce scaling weight.

Irrespective of whether the cooling process uses refrigerated air or saturated air, an increase in heat transfer rate to the bread (or baked product surface) can be achieved by ensuring adequate spacing between loaves. Spacing is important to achieve good heat transfer from the moving air to the bread surface. This was demonstrated using a simple computational fluid dynamics model (CFD) with bread loaves represented by solid blocks (Thorn 2001). All fluids take the path of least resistance and so air will flow around the blocks of bread unless the gaps between blocks are sufficient for it to pass through. It is counterintuitive to increase spacing between loaves in a cooler because this would appear to reduce the quantity of bread that can be cooled. However, the increase in heat transfer rate to the surface more than compensates for this.

Further reduction in cooling rates can be achieved by cooling under vacuum conditions. A small number of commercial systems have been introduced to affect this; however, none have widespread uptake and most have since been abandoned. The Tweedy Modulated Vacuum Cooling system (MVC) is still used for malt loaves in which the loaves are transferred from the oven to a vacuum chamber before the crumb has set fully. Application of a vacuum results in latent heat being released at a temperature lower than 100 °C with the result that the loaf interior is converted from its dough state into a crumb. Baking time must be reduced to avoid over-baking, and in this case it is reduced by around 28%. Cooling takes 60 s in unlidded tins or 78 s in lidded tins (Bradshaw 1976). The Milton Keynes process was introduced to provide ambient pre-formed bread for bake-off by the retailer. Sainsbury, APV Baker, Kears Group, and Gist Brocades were the four partners who initiated this process in 1995 (Cauvain 2012). Baking was a deliberately slow process in a steam tunnel followed by a short convective section. The bread was not fully baked when it left the oven although the starches were gelatinized or close to full gelatinization. Crumb water content was high as the bread left the oven. Vacuum cooling removed more water than conventional cooling, and was reported to stabilize the crust strength. Cooling times to 30 °C were 4–5 min compared with 90–100 min for conventional cooling. Bake-off by the retailer or customer provided crust color and corrected the water content.

Summary

This chapter has described how processing of baked products involves a sequence of processing stages that starts with mixing and ends with cooling. A structured process optimization study must consider all stages as linked stages because changes to any one processing stage will affect other stages as a result of the interactions between stages. For example, increasing the proofing temperature will change the gas cell expansion of bread dough and also affect the baking process because of changes this imposes to the heat and mass transfer. Additional difficulty in optimizing the bread making process is the time from start of mixing to end of baking and how to ensure changes made to one stage are not compromised by another. These create challenges for process optimization and make the subject interesting.

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22

Sensory Attributes of Bakery Products

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Introduction to basic principles in sensory assessment

In order to better understand, optimize, and tailor the sensory characteristics of cereal materials, it is important to recognize certain basic principles and influencing factors in sensory perception. Sensory analysis is "a scientific discipline used to evoke, measure, analyse and interpret reactions that are the characteristics of foods and other materials as they are perceived by the senses of sight, smell, taste, touch and hearing" (Stone and Sidel 2004). Sensory evaluation is a multidisciplinary challenge that requires an understanding of food science, statistics, chemistry, nutrition, physiology, and psychology.

Sensory attributes and senses

Appearance, odor, texture, and flavor are important attributes in determining the overall characteristics of a product ([Figure 22.1](#)). Traditionally these attributes are evaluated independently of each other by receptors of the different senses, although the possibility of a multimodal perception by human beings has recently been suggested. Sensory assessment is based on perception, using the senses of vision, touch, olfaction, gustation, and hearing. In addition, chemical irritants such as menthol, pepper, or ammonia stimulate trigeminal nerve ends, causing such sensations as cold, heat, pungency, burning, or tingling.
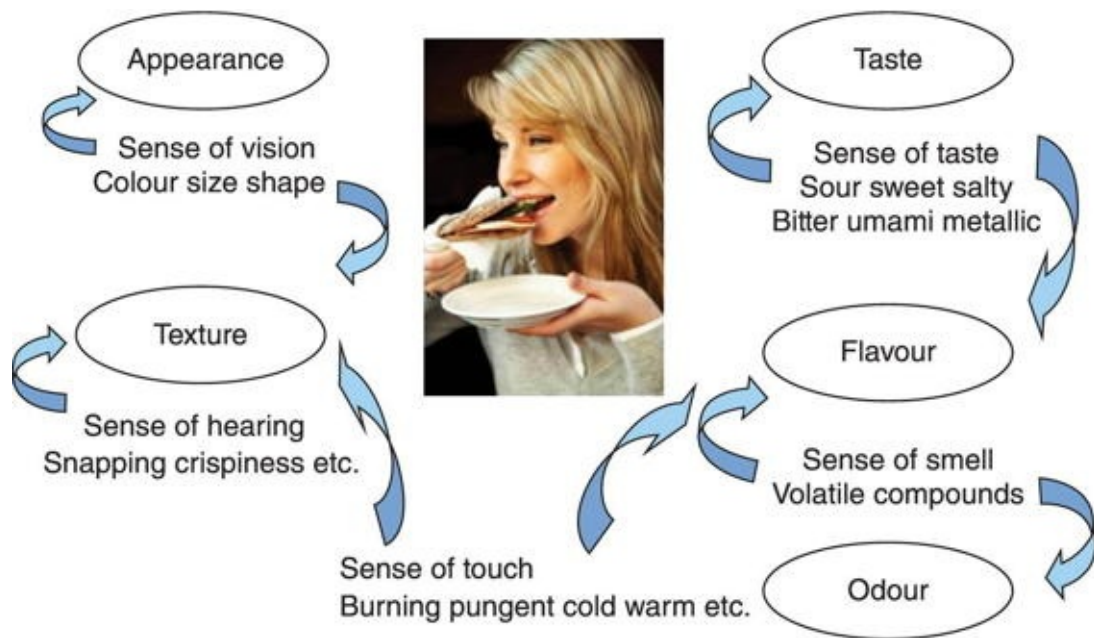
Figure 22.1 Senses used in multimodal sensory perception of foodstuff attributes. (Photo courtesy of VTT Technical Research Centre of Finland).

The sense of sight is used in evaluating appearance, for example, the color, shape, or size of a product. Sight, touch, and hearing, in combination, are important in perception of texture, for example, crispiness, juiciness, or softness. The taste receptors are located on the surface of the tongue, clustered into taste buds, and saliva is necessary as a carrier for taste perception. The classical four basic tastes include sweet, salty, sour, and bitter, but suggestions to add umami and metallic have been widely accepted. The interactions of the four basic tastes, especially at different concentrations, are complicated. For example, at moderate concentrations salts and acids are known to enhance each other, but at high concentrations they suppress each other's effect. Volatile compounds in the headspace of the product are

sensed by the olfactory receptors located very high in the nasal cavity. This diversity is mediated by smell, and the olfactory perception is based on the transduction mechanism. Usually when talking about taste, we actually mean flavor, as related to retronasal perception. Flavor is the simultaneous perception of taste, odor, and trigeminal nerve response (Lawless and Heymann 2010).

Volatile and non-volatile chemical compounds must exceed their specific odor or taste thresholds to be perceived. The thresholds may be categorized into detection, recognition, difference, and terminal thresholds, depending on their perception intensity (Meilgaard and others 1999). For example, the odor perception of a product is caused by several different volatile compounds, and their relative amounts in the headspace dominate perceived odor. Note also that a wide variation between thresholds exists within and between individuals. Different types of odors and tastes tend to mask or suppress each other, which is often called mixture suppression. On the other hand, tastes may also increase the apparent intensity of odors, or odors may increase the apparent intensity of taste (Noble 1996).

Regarding the perceived flavor, knowledge of phenomena involved in the complex flavor release is crucial (Plug and Haring 1994; Laing and Jinks 1996; Taylor 1996; Taylor and Linforth 1996; Buettner and Schieberle 2000; Dattatreya and others 2002; Linforth and others 2002). In general, while eating, flavor perception is determined by the nature and amount of the flavor components, the availability of these to the senses as a function of time, and the mechanism of perception. The flavor release is influenced by the individual shear-force during chewing, saliva volume and composition, breathing rate and volume, diffusion of molecules, binding, the pH of the solution, and the solubility of the flavor molecules. In addition, the stimulus caused by the flavor compound varies depending on the chemical and physical properties of the volatile substances; the texture, shape, and hydrophobicity of the material; interactions between the food components; and the state of the food (Guichard 2002). Through understanding the mechanisms by which the flavor compounds are formed, flavor formation may be controlled by optimized methods of food processing.

General requirements for sensory assessment

General instructions for organizing sensory evaluations are well described in the textbooks (Meilgaard and others 1999; Stone and Sidel 2004; Lawless and Heymann 2010) and ISO standards dealing with the topic. Thus, only the key issues in organizing sensory assessments are reviewed here.

A trained panel is the objective instrument used in sensory assessments, and it must be clearly distinguished from the hedonic or acceptance evaluations performed by subjective consumer panels. Special attention should be paid to recruiting and pretesting of assessors. Frequent monitoring of the panel's performance and the motivation of the panelists is crucial for getting reliable results. The size of the panel should be large enough, depending on the experience of assessors, the method used, and the product to be evaluated. Individual differences between the subjects of a sensory panel should not be ignored. This is the main reason for using large sensory panels. In the test facilities, a specific area should be allocated for sensory evaluation. For sample presentation, the samples should be blind-coded and served in a balanced, random order to the assessors.

In general, analytical sensory methods can be roughly divided into several types of difference

tests and descriptive analysis. They must be clearly distinguished from affective consumer tests, that is, acceptability, preference, and hedonic response studies. The choice of the sensory method depends on the aim – What, in the end, do you want know about the product? The sensory characteristics of cereal products are usually determined by descriptive analysis (descriptive profiling), which gives a comprehensive view of the most important perceived attributes of the products (Stone and Sidel 1998, 2004; Meilgaard and others 1999; ISO 2003; Lawless and Heymann 2010). The vocabulary used is therefore characteristic of each specific product and must be created separately. Sensory profiling describes the relative distances between the products for each attribute. The selected attributes of the sensory profile describe the appearance (including color), odor, flavor, and texture characteristics of the different products as extensively as possible.

Sensory attributes of bakery products

Flavor, texture, and color are the salient general attributes of cereal products. The product will certainly fail on the market if one of these general attributes does not meet the expectations of consumers. Attempts to create general vocabularies (Hayakawa and others 2010; Callejo 2011; Elía 2011) and common evaluation procedures (Elía 2011) for descriptive analysis of bread have recently been made. However, each product has its characteristic sensory profile with specified attributes. For example, a roasted flavor is an especially important attribute in bread and other cereal products; crispiness is a characteristic texture attribute for several dry bakery products. Heenan and others (2008) described the bread freshness by relating the sensory profile of wheat bread to consumer perceptions.

The ingredients – flour, liquid (water), yeast, salt, sweetening agents, fat, emulsifiers, eggs, milk powder, and spices – used in baking have their own effect on the sensory characteristics of the end product. In addition to the raw materials and flavor precursors, the processing of grains considerably changes both the flavor-active compounds and the perceived flavor. Although processing is often considered to be a negative attribute from the nutritional point of view, processing of grains is necessary prior to their consumption. Processing must provide products that have a suitable form and good sensory properties.

Grain and flour

In general, wheat, maize, and rice are the leading cultivated grains worldwide, but other minor varieties of cereal such as rye, oat, and barley should not be ignored. Each variety of grain has its characteristic flavor; for example, the oat-like flavor is milder than the rye-like flavor. Grains have their own effect on the flavor; for example, oat grain or meal often gives a nutty flavor to a cereal product. The grain cultivar also influences the flavor. The chemical composition of native grains varies significantly depending on the growing environment, the genotype, and their interaction. These may substantially contribute to the perceived flavor indirectly; for example, the nitrogen content of the soil greatly influences the composition of amino acids and, as a result, the protein composition of the grain. Variations in the composition may also arise from differences in harvesting and postharvesting conditions, or in the treatment of the grain prior to its use. The specific season is a dominant factor (Kihlberg 2004), especially for protein and fat production.

The flavor of native, untreated grain is very mild and bland. Very little literature is available on the perceived flavor of native grains, whereas the flavor of processed cereal products is far better documented. The reason for this might be that native grains are not used as such: some kind of processing is always required before their consumption.

In mechanical *milling fractionation* the kernel is separated into endospermic, shorts, and bran fractions. The flavor components are unevenly distributed in the kernel (Heiniö and others 2003a). Between the mild-tasting innermost, endospermic part of rye grain and the bitter-tasting outermost bran fraction, a rye-like flavor without any obvious bitterness is observed. This fraction also contains significant amounts of bioactive compounds, such as alk(en)ylresorcinols and phenolic acids (Heiniö and others 2008). The aleurone layer of a grain contains many enzymes, including peroxidases, polyphenoloxidases, and amylases.

When the aleurone layer is damaged during milling, off-flavor development, pigment darkening, and starch breakdown may result. Foods become gray when polyphenoloxidases convert colorless phenolic compounds to dark polymers. The use of hydrogen peroxide to bleach the dark color of grains is patented (Metzger 2003), but the possible loss of phytochemicals is not known. The milling technique has a greater impact on the sensory quality of whole-grain wheat than the baking technique: bread baked with roller-milled wheat was described as being sweet, juicy, and compact, with a small slice area, whereas bread baked with stone-milled wheat was salty, deformed, and roasted (Kihlberg 2004).

Bread

The trends in the relative popularity of different types of breads are reflected in their consumption volumes. For the consumer, the key attributes of bread are flavor and texture. The degradation of the taste of bread is related to modern manufacturing techniques and the speed of large-scale bread production (Wirtz 2003). However, the flavor and stability of the texture may be improved by using predoughs containing yeast or lactic acids. In addition to large-scale production, smaller local bakeries produce their own special breads. Regional, ethnic, socioeconomic, and even gender or age factors also determine which types of breads are produced.

Apart from the main constituents of flour, sugar, yeast, and salt, other ingredients of bread influence the flavor very little. Most of the flavor develops from these raw materials during dough processing and baking. The flavor of bread is formed in processing through oxidation and enzymatic and thermal reactions. Volatile compounds evaporate in oxidative reactions. Enzymes produce flavor precursors in dough processing and in the early stage of baking. The most important flavor compounds of bread are formed during baking, when heat reactions, such as the Maillard reaction and caramelization, take place. Enzymatic and possible fermentation reactions influence the flavor of bread crumb, whereas heat reactions affect the flavor of bread crust. As a result, the crust and crumb of bread have different flavor properties (Schieberle and Grosch, 1985, 1994; Kirchhoff and Schieberle 2001).

The composition of flour is two-dimensional. Some chemical compounds, such as amino acids, fatty acids, and phenolic acids, act as flavor precursors, forming flavor-active compounds during baking, whereas some volatile compounds in flour affect the perceived flavor. Sugars give a slightly sweet note to bread, but they are also important flavor precursors. During baking, in conjunction with free amino acids, they give a roasted note to the bread, through the Maillard reaction. Yeast breaks down sugars in dough fermentation to alcohol and carbon monoxide, and flavor-active compounds, such as alcohols, organic acids, esters, lactones, and carbonyls, are formed as secondary fermentation products.

Salt-free bread has a bland taste. Thus, salt is used in breads for improving the taste, texture, and stability, and for strengthening its flavor. As a result, consumers have acquired a taste for bread with added salt even though nutritional guidelines still recommended that salt intake be reduced. The taste of salt-free food may not, at least initially, meet consumers' expectations, and therefore eating habits may take time to change. Sourdough fermentation is used in rye and wheat bread processing, and it increases the sourness of the bread. At high NaCl concentrations, the saltiness and sourness of rye bread tend to compete with each other, and saltiness can be masked by sourness (Barylko-Pikielna and others 1990; Hellemann 1991; Heiniö and others 1997). Consequently, the NaCl concentration could be substantially

lowered without significant change to the sour rye bread flavor. The perceived sourness of rye bread is strongly related to the concentrations of lactic and acetic acids (Hellemann and others 1988).

As well as its flavor attributes, the overall perception of bread is dramatically influenced by its freshness, color, texture, and biting properties . In particular, softness, which is characteristic of fresh bread, decreases quickly during storage. Fat addition, if used, softens the bread crumb, stabilizes texture, and improves the bread volume, but also improves the perceived flavor by forming carbonyl compounds during the baking process. Breads made with whole-grain flours often have reduced loaf volume, dense crumb, reduced crumb softness, and a dark crumb and crust.

Flavor formation may be influenced not only by the ingredients, but also by dough processing. Vigorous mixing produces considerably higher levels of acetic and several other acids than conventional mixing, probably due to over-oxidation of the dough (Wirtz 2003). Dough leavening can also indirectly influence flavor formation because it often determines fermentation time. The temperature is important during baking. Both the Maillard reaction and caramelization occur on the bread surface at about 230–250 °C, while the crust temperature only slightly exceeds 100 °C. Then the bread crust will get toasted, nutty, and frying notes together with a characteristic color. However, if the baking temperature is too high, bitterness develops and the color will be too intense.

Crispness is the most salient texture attribute of crisp bread. The flavor of crisp bread resembles that of soft bread, although the manufacturing processes are significantly different. Crisp rye bread contains significantly more aromatic compounds (about 25%) than soft rye bread (less than 10%), most of these compounds originating from the Maillard reaction.

The salient descriptors of bread qualities depend on the ingredients and the process applied. In general, common flavor attributes for bread are intensity of cereal flavor in crumb and crust, sweet, toasted/roasted, fresh flavors, and in sourdough fermented breads, bitterness. Common texture attributes for breads are softness, moistness, and springiness. Some examples of sensory descriptors of different types of breads are given in Table 22.1.

Table 22.1 Examples on sensory attributes of bread

Cereal product	Sensory attributes	Scale	Reference
Oat bread	**Visual texture**: Volume, pore size, uniformity of pore size **Mouthfeel of crumb**: Moistness, softness, density, crumbliness, springiness	10-point, verbally anchored intensity scale	Salmenkallio-Marttila and others 2004
Wheat bread	**Appearance**: Colour **Aroma**: Wheat, cereals, earthy **Texture (by finger)**: Elasticity, compressibility, deformability **Texture (mouthfeel)**: Juiciness **Flavour**: Wheat, cereals, earthy, astringent	100-point, continuous, unstructured intensity scale	Kihlberg and others 2005
Wholemeal	Elasticity, colour, acidulous smell, acidulous	100-point,	Haglund and

wheat bread with ascorbic acid additions	taste, sweetness, dryness, aroma	verbally anchoredintensity scale	others 1998
Wheat sourdough bread	**General terms**: beer, burnt, butyric, caramelised, dairy impression, doughy flavour, eggy, fruity, leavening, musty (dusty, old leather), musty (earthy, damp), nutty, oily, olive oil, sweet aromatics, toasted, wheat, yeasty; **Sour characteristics**: sour aromatics, dairy sour, lemon, malic acid, vinegar; **Fundamental taste**: bitter, salty, sour, sweet; **Mouthfeel**: astringency, chalky mouthfeel, oily mouth coating, tongue numbing and toothetch	15-point intensity scale anchored with reference foods	Lotong and others 2000
Wheat sourdough bread	**Texture**: Softness, springiness, moistness of bread crumb **Flavour**: Degree of roasted flavour of bread crust, pungency, freshness, overall flavour intensity and aftertaste intensity of bread crumb	10-point, verbally anchored intensity scale	Katina and others 2006
Rye sourdough bread	**Appearance**: Darkness of crust, darkness of crumb, cracking of crust, floury crust, leavening, porosity **Odour**: Overall aroma, musty, burnt, rye-like, malty, sweetness, sourness **Taste**: Overall intensity, sweetness, saltiness, sourness, bitterness, burnt, flour-like, rye-like **Texture**: Hardness of crust, hardness of crumb, moistness, graininess, toughness, chewiness **Overall impression**: Freshness, pleasantness	10-point, verbally anchored intensity scale; consumer panel regenerating vocabulary in pairwise presentations	Hellemann and others 1987
Rye sourdough bread	**Odour**: Overall intensity, sweetness, sourness, rye-like **Taste**: Overall intensity, sweetness, saltiness, sourness, bitterness, flour-like, rye-like **Overall impression**: Desirability	10-point, verbally anchored intensity scale	Hellemann and others 1988
Rye sourdough bread	**Appearance**: Colour intensity **Texture & mouthfeel**: Softness, springiness, moistness, coarseness **Flavour**: Flavour intensity of crust,	10-point, verbally anchored intensity scale	Heiniö and others 2003a

	freshness, cereal flavour, bitterness, flavour intensity of crumb; aftertaste intensity Hayakawa and others 2010		
Wheat bread (freshness)	Vocabulary consisting of 28 descriptive attributes for appearance, odor, flavor, oral-texture and after-flavor of bread	Unstructured 100 mm line scale, labeled low (5 mm) and high (95 mm)	Heenan and others 2008
Bread	Common vocabulary consisting of 23 descriptive attributes for appearance, aroma, taste and texture of bread	5-point, verbally anchored intensity scale	Hayakawa and others 2010
Bread	Review: Several attributes for appearance, odor, texture and flavor of bread	Several scales	Callejo 2011
Bread	Common vocabulary consisting of 46 descriptive attributes for appearance, aroma, taste and flavor and texture of bread	10-point, linear, continuous, verbally anchored intensity scale	Elía 2011

Breakfast cereals

Flaked grains for ready-to-eat cereals and milled grains for hot cereals (mainly porridges) are counted as breakfast cereals. Grains may be used intact, coarsely ground or cut, or milled to flour. The processes involved in producing ready-to-eat cereals include rolling, flaking, extrusion, gun puffing, shredding, baking, or a combination of these, all of them influencing the perceived sensory attributes of the products. These processes often require moisture and heat to form a crispy, crunchy texture, which is one of the most desirable attributes in ready-to-eat breakfast cereals. In hot cereals the grain may be precooked or unprocessed, and together with the flavor attributes, other texture attributes, such as thickness and viscosity, are important in them.

Whole-grain cereals with a bran layer are darker in color than products made from grains without bran. Wheat, corn, oats, rice, barley, or even flaxseed, triticale, buckwheat, or rye may be used as cereals. In addition to cereals, other ingredients influencing the sensory characteristics are used. Soy protein can give a slight nutty flavor. Malt extract and sweeteners, such as liquid sugar, sucrose, cane juice, molasses, honey, syrups, or concentrated fruit juices, in addition to their characteristic flavor, have a role as flavor precursors in the Maillard reaction, contributing a roasted flavor and dark color. Oil may act as a flavor carrier or improve texture and texture retention. Fruit, berry, raisin, nut, and seed additions give their own characteristic flavor to the breakfast cereal. Flavors are best applied as part of a sugar coating on the cereal. "Brown" flavors are common in cereals, and are not as susceptible to volatilization as, for example, fruit flavors.

Other cereal products

As well as bread and breakfast cereals, a wide variety of other bakery products, such as pastries and cakes, are available on market. These include different types of pies, rusks,

coffeebreads (with and without yeast), doughnuts, confectionery products, shortcakes, cookies, and biscuits. The amount of cereal ingredients in some of these products may be rather small, and therefore other ingredients, which are too variable to be described in this context, have a considerable influence on their sensory characteristics. In addition, some national specialities among cereal products exist. For example, azyme is a very thin wheat bread from Scandinavia that is not fermented and has a slightly bitter taste. Various cereal products made from sorghum are typical in Africa (Anyango and others 2011).

Related to the increasing interest in partly prepared, convenience foods, the market for prebaked frozen cereal products, which are baked at home, is constantly growing. It is possible to achieve many desirable sensory attributes, such as a fresh, cereal flavor, crisp crust, and soft crumb, using this technology.

Factors affecting sensory attributes of bakery products

In addition to simply measuring the sensory profiles of products, the basis for the sensory quality of bakery products should lie in actively designing the sensory attributes found most attractive by consumers (Figure 22.2). Using different processing techniques and knowing their influence, the flavor and texture of the products may be adjusted in the desired direction (Heiniö and others 2011). An example spider plot of a descriptive sensory profile of breads processed in different ways is presented in Figure 22.3.
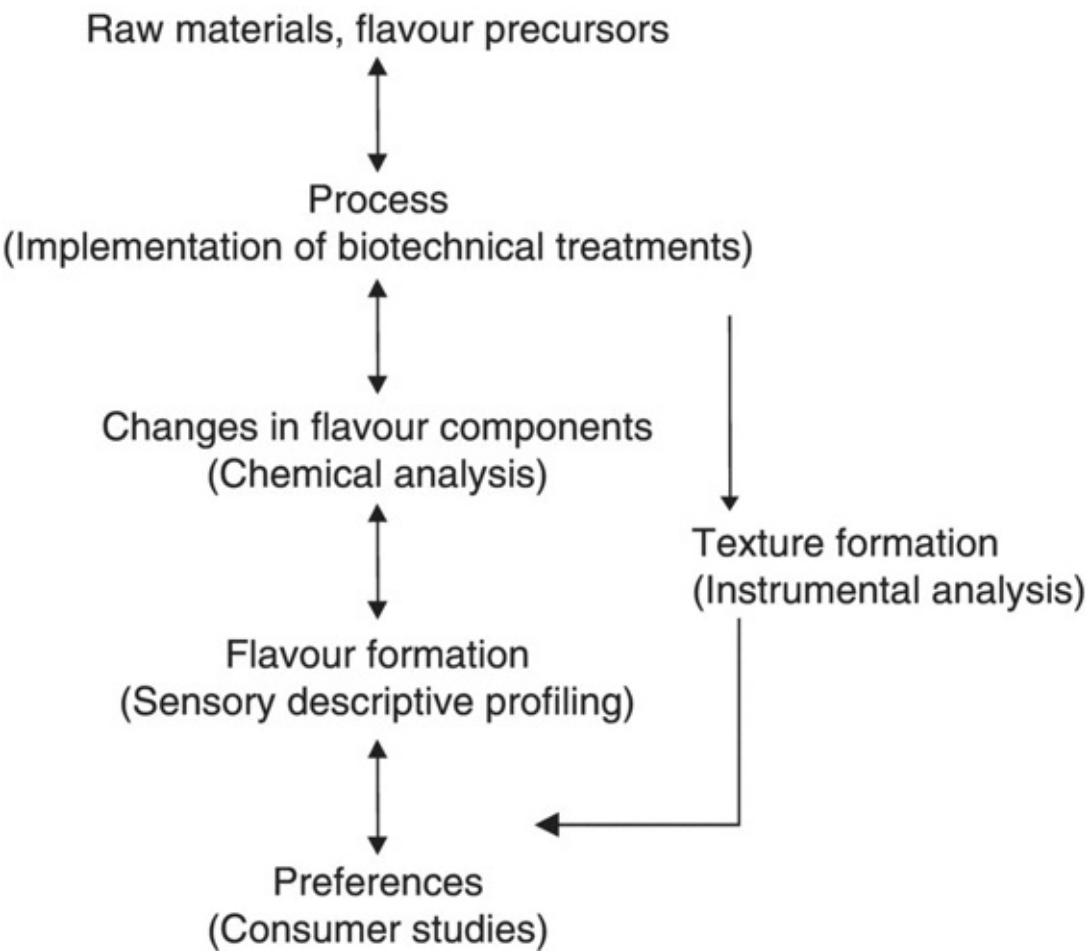
Figure 22.2 Formation and determination of flavour and texture of cereal products.
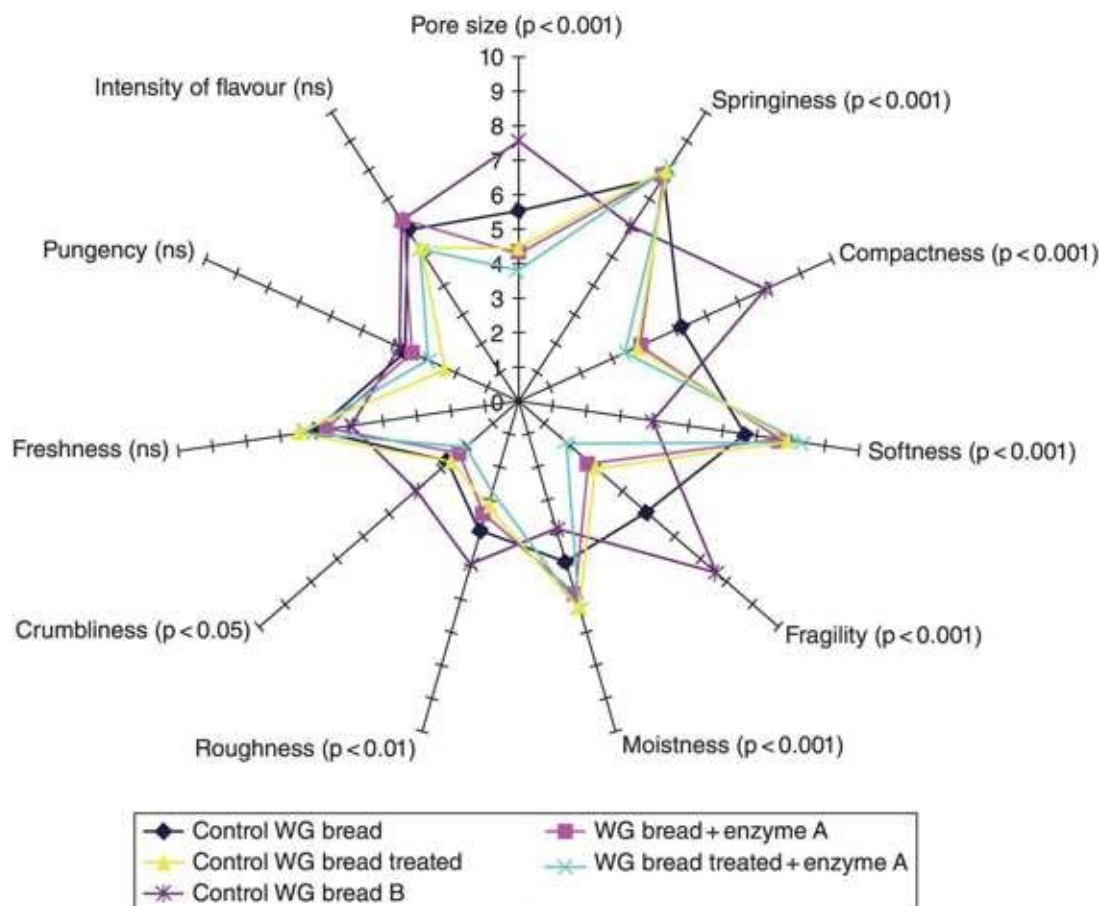
Figure 22.3 Descriptive sensory profile of bread samples.

Influence of bioprocessing on sensory characteristics

Cereal flavor forms mainly during processing, and the relatively plain flavor of native grain may be considerably adjusted by different bioprocessing techniques (Heiniö 2003; Heiniö and others 2012). At the same time, bioprocessing may increase the amounts of phenolic compounds and vitamins. One of the most effective ways of modifying flavor is through heating. On the other hand, enzymatic reactions, such as the oxidation or hydrolyzation of lipids, may take place and result in undesirable flavor notes. Sensory attributes may be related to certain volatile and non-volatile compounds, often specific to each processing technique. Some examples of sensory attributes of processed grains are given in Table 22.2.

Table 22.2 Examples on sensory attributes of processed grains

Cereal product	Sensory attributes	Scale	Reference
Fractionated rye flour	**Flavour:** Cereal flavour, freshness, sweetness, bitterness, germ-like flavour, rancidity, flavour intensity, aftertaste intensity	10-point, verbally anchored intensity scale	Heiniö and others 2003a
Cooked rice	**Aroma:** Sewer-animal, floral, grain-starchy, haylike-musty, popcorn, corn, alfalfa-grassy-green bean, dairy, sweet, aromatic **Taste:** Sweet, sour-silage	15-point, verbally anchored intensity scale	Champagne and others 1997

	Feeling factor: Astringent, waterlike-metal		
Cooked oatmeal	**Odour**: Overall intensity, toasted **Manual texture**: Thickness, adherence to spoon **Flavour**: Overall intensity, toasted **Oral texture**: Average size of swollen flake particles, uniformity of mass, slipperiness, coarseness **Appearance**: Darkness of colour	10-point, verbally anchored intensity scale with reference subtances	Lapveteläinen and Rannikko 2000
Heat treated oat grains	Odour intensity, flavour intensity, rancid odour, fresh odour, fresh flavour, oat odour, oat flavour, sweetness, bitterness, aftertaste, hardness, crispiness, greasiness, stickiness	9-point continuous, unstrutuctured intensity scale	Molteberg and others 1996
Germinated, dried oat	**Odour**: Cereal, roasted, moist, musty, earthy, intense **Flavour**: Cereal, roasted, nutty, sweet, bitter, germ-like, musty, rancid, intense; aftertaste **Texture**: Hard, tough, moist, crisp, brittle	10-point, verbally anchored intensity scale	Heiniö and others 2001, 2002
Native, germinated and sourdough fermented rye after extrusion	**Flavour**: Cereal flavour, freshness, sweetness, sourness, roasted flavour, flavour intensity; aftertaste intensity **Texture**: Porosity, crispness, hardness, toughness	10-point, verbally anchored intensity scale	Heiniö and others 2003b
Extruded maize and wheat flour	Burnt, sugar puffs, nutty, bran-like, toasted, puffed wheat, cooked vegetable, porridge-like, cooked milk, popcorn, stale, fermented, meaty, bready, sweet, malty, cornflakes	100-point, anchored intensity scale	Bredie and others 1998
Rice	Vocabulary consisting of 25 descriptive flavour attributes	15-point numerical intensity scale	Bett-Garber and others 2012
Sorghum foods	Vocabulary consisting of 17 descriptive attributes for appearance, aroma, texture, flavor and sensations after swallowing the sample	10-point, verballyanchored intensity scale	Anyango and others 2011
Several oat products	Review		Heiniö and others 2011

Sourdough fermentation is applied to rye prior to baking the dough into bread, although it is also optional in baking wheat (Rizzello and others 2012). Although not used worldwide, rye is an important cereal in the German, Polish, Russian, and Nordic diets in particular, and is

traditionally consumed as soft bread or in the form of crisp bread. The flavor of pure rye flour is rather mild. The typical strong, sour, and slightly bitter flavor of rye bread is formed during sourdough fermentation, which is necessary for rye bread production (Hellemann and others 1987, 1988). The bitterness does not decrease even after a heat treatment, such as extrusion or baking (Heiniö and others 2003b). Concurrently, the amounts of lactic and acetic acids increase. Sourdough fermentation strengthens the sour flavor and produces flavor components mainly in the bread crumb, whereas the baking process mainly influences the flavor of the bread crust, resulting in a roasted flavor. The sourness of bread can reduce the amount of salt used in baking it (Hellemann and others 1988; Hellemann 1991; Heiniö and others 1997). The pungent flavor that develops in sourdough fermentation of wheat bread can be minimized by using process optimization (Katina and others 2006).

The oxidation of lipids and enzymatic and heating reactions are the key reactions influencing the flavor formation of rye bread (Hansen and others 1989; Schieberle 1996). Volatile compounds evaporate from flour as a consequence of oxidation reactions. Enzymatic reactions produce flavor-active compounds both during sourdough fermentation and at the beginning of baking. The flavor compounds produced during the baking process are possibly the most essential compounds for the flavor of rye bread, and they mainly form during the heat treatments.

To date, *germination* has mainly been used for barley in beer production, but it can also be an effective method of adjusting the flavor of other cereals, such as oat and rye (Heiniö and others 2001, 2003b). In general, moisture, temperature, and germination time are the major variables in germination, which is completed by a drying process. These fundamentally affect the flavor profile of grain. Germination initiates the bioactivity of the grain and results in the formation of new flavor components. Germinated grains are a good source of free amino acids and sugars, which act as flavor precursors for the flavor-active compounds. The flavor profile of native barley is changed in germination from fruity and haylike to the burnt, breadlike, malty, and chocolate-like flavor of germinated, dried barley (Beal and Mottram 1993). The toasted and cereal-like flavor has also been found in heat-treated oat flakes (Sides and others 2001). The roasted, sweet, and nutty characteristics can clearly be related to such volatile compounds as dimethyl sulfides and isobutanol (Heiniö and others 2001).

The grain flavor and texture may be considerably modified by several *thermal-processing techniques*, such as germination and subsequent heat treatment, extrusion cooking, autoclave, puffing and roasting techniques, or microwave heating. All of these have a high processing temperature in common, although any possible pretreatment prior to heating may also significantly influence the flavor.

The *Maillard reaction* is one of the major reactions influencing the flavor and color of a product (Fayle and Gerrard 2002). It consists of several complex reactions, and not all of which are yet known in detail. Heat and dry atmosphere accelerate the Maillard reaction. At high temperatures, free amino acids or small peptides together with free sugars are especially important flavor precursors, since they form volatile flavoring compounds such as heterocyclic pyrazines, pyrroles, furans, and sulfur-containing compounds. These compounds are abundant in high-temperature, low-moisture extruded oats, and the products are described as roasted or toasted, caramelized and somewhat sweet, or nutty in flavor (Heydanek and McGorrin 1986; Parker and others 2000).

Extrusion is a continuous process using both temperature and pressure for extrusion blowing

of a flour–water suspension. It is used in preparing puffed and flaked ready-to-eat breakfast cereals, savory and sweet expanded snacks, croutons, bread crumbs, crisp flatbreads and breadsticks, and rice and pasta substitutes. It increases product darkness, due to the Maillard reaction and enzymatic browning of phenolic acids. So far it has mainly been applied to wheat, but applications for oats have also been reported (Pfannhauser 1993; Sjövall and others 1997; Parker and others 2000; Reifsteck and Jeon 2000; Bredie and others 2002). As a heat treatment, it is very effective in modifying the cereal flavor, resulting in a roasted flavor and crispy texture. Temperature and moisture level are important factors in flavor formation of extrusion products (Bredie and others 1998). Extrusion products are susceptible to oxidation due to the increased surface area and the denaturation of lipoxygenase and other enzymes involved.

The use of *enzymes* in manufacturing bakery products is a novel technology for modifying the flavor and texture (Heiniö and others 2012). In particular, hydrolytic enzymes could be applied in the future for breaking down the cell walls or other constituents of the grain. For example, the addition of amylase retards staling of bread by preventing starch retrogradation. Xylanase, proteases, lipases, and oxidases are other useful bakery enzymes.

Influence of storage on sensory characteristics

Cereal products easily become stale when stored. Two main factors influence the deterioration of the quality of cereal products: rancidity of the flavor and dryness of the texture. Textural changes, for example, bread drying out, can be avoided to some extent by using suitable packaging solutions, whereas for unpacked products, modifications of the recipe are necessary.

Grains with a high fat content, such as oat (fat content 4–6%), are susceptible to lipid oxidation after processing, when the antioxidants of the grain are damaged. Flavor deterioration during storage may result from both volatilization of desired flavor attributes and the development of undesired off-flavors. A bitter off-flavor and rancidity, in particular, are easily formed in unprocessed oats during storage. The sensory perceptions of these rancid and bitter off-notes result from the oxidative or hydrolytic degradation of lipids of a grain, although deterioration of proteins and reactions of phenolic acids should not be excluded. Oxidative rancidity develops as a result of enzymatic and non-enzymatic processes. Accordingly, the hydrolytic rancidity is a result of lipase activity in the outer layers of the grain, where fat degrades to free fatty acids (Welch 1995). A high moisture level, light, an elevated storage temperature, and a high oxygen concentrations increase the development of rancidity (Ekstrand and others 1993; Molteberg and others 1996; Larsen 2002). The development of rancidity can be prevented or decreased by heat treatment; phenolic compounds, such as avenanthramides and caffeic acid (Molteberg and others 1996); or the germination-drying process (Heiniö and others 2002).

Chemical agents

The flavor of cereal products results from a mixture of several chemical compounds (Figure 22.4). The composition of a grain or cereal product may directly influence the perceived flavor in two ways: (i) through certain volatile compounds, such as aldehydes, ketones, and alcohols, in the airspace of a product; and (ii) through nonvolatile compounds, such as

phenolic compounds, sugars, amino acids and small peptides, free fatty acids, and lipids. This second group may also indirectly influence perceived flavor, acting as flavor precursors through reactions that form various new flavor compounds in the product during processing.
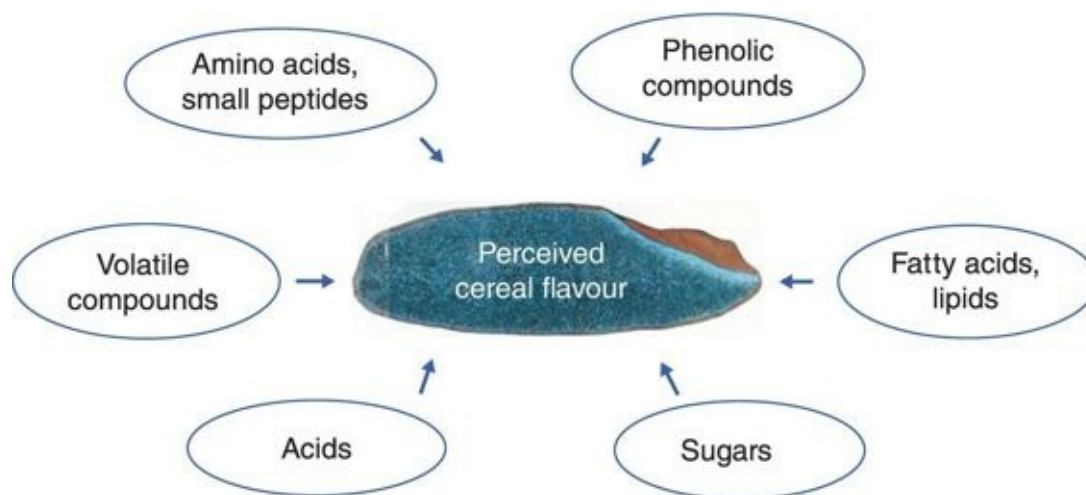
Figure 22.4 Chemical components of grain influencing the perceived flavour. Volatile compounds (odour) influence as such, non-volatile compounds (flavour) as such or as flavour precursors.

Similar *volatile compounds* are found both in native and processed grains, and the main difference seems to be in the amounts and relative proportions present in the products. Some volatile compounds are dominant in both, that is, aldehydes, ketones, and alcohols, but as a result of heat treatment, derivatives of pyrazines and pyridines are also often found. In general, untreated grain or flour contains small amounts of just a few flavor-active compounds (Hansen 1995). These compounds are often aliphatic aldehydes, such as pentanal and hexanal, formed as oxidation products from fatty acids, and the corresponding alcohols, pentanol, and hexanol. Some of the carbonyl compounds possess a green odor note, with a pungent flavor.

Numerous new volatile compounds are formed during the grain processing (Pozo-Bayón and others 2006). Although they are often identical compounds, their amounts and relative proportions may vary significantly depending on the process parameters, thereby resulting in different flavors. Important flavor compounds in rye sourdough are alcohols, esters, and carbonyls (Hansen and others 1989; Lund and others 1989). In baking, mainly compounds related to the Maillard reaction form: alcohols, acids, aldehydes, hydrocarbon-substituted furans, ketones, lactones, pyrazines, hydrocarbon-substituted pyrroles, and sulphur compounds. The perceived flavor and the flavor-active volatile compounds of the crumb are significantly different from those of the crust in rye bread (Schieberle and Grosch 1985, 1994; Grosch and Schieberle 1997; Kirchhoff and Schieberle 2001) and may be effectively influenced by modifying the process parameters in sourdough fermentation and baking. In germination, different types of volatile compounds form at low processing temperatures and high moisture levels as compared with those formed at higher temperatures and lower moisture levels. After kiln drying, oat flavor components, such as terpenes, alkylbenzenes, aldehydes, alcohols, and heterocyclic compounds, develop (Dimberg and others 1996). In extruded oat, compounds form from the Maillard reaction (for example, pyrazines, pyrroles, furans, and sulfur-containing compounds with toasted sensory descriptions), and from lipid oxidation (for example, hexenal and hexanol) (Pfannhauser 1993; Sjövall and others 1997; Parker and others 2000). The high extrusion temperature and alkalinity of the system

significantly influence the flavor generation from wheat flour by forming nitrogen-sulfur-containing heterocyclic compounds described as being sulfury and rubbery in odor (Bredie and others 2002).

The reduction of desired flavor attributes through volatilization and development of undesired off-flavors influence flavor deterioration of cereals during storage (Zhou and others 1999). The long-chain hydroxy fatty acids cause a bitter taste perception. Aldehydes, ketones, and alcohols cause rancid flavor, hexanal being the most dominating. However, rancidity is due as much to a change in the concentration of hexanal as to its absolute presence (Sides and others 2001).

Many *phenolic compounds* exhibit antioxidative activity, and some of them may be salient in defence against diseases (Welch 1995; Decker and others 2002). Non-volatile phenolic compounds, such as phenolic acids, lignans, avenathramides, and alk(en)ylresocinols, often contribute considerably to the flavor of cereal products (Dimberg and others 1996; Weidner and others 1999; Heiniö and others 2008). The most abundant phenolic acid in cereals is ferulic acid, but others, such as sinapic, *p*-coumaric, syringic, and caffeic acids, are also essential (Welch 1995; Weidner and others 1999; Liukkonen and others 2003). Free phenolic acids may influence the flavor perception in very small amounts, 10–90 mg/kg (Dimberg and others 1996). Some phenolic compounds (*p*-coumaric acid, vanillin, *p*-hydroxybenzaldehyde, and coniferyl alcohol) may also contribute to the rancid, bitter, intense flavor of oat (Molteberg and others 1996). In rye grain, the 5-alkylresorcinols (5-alkyl-1,3-dihydroxybenzenes) are important phenolic compounds (Shewry and Bechtel 2001).

Free *amino acids* and especially small *peptides* may influence the perceived flavor as such or as flavor precursors. In general, amino acids form flavor-active volatile compounds, such as pyrazines, pyrroles, and furfurals, as a result of the Maillard reaction at high temperatures. Proteases produce amino acids or peptides in the product. Amongst amino acids, ornithine, phenylalanine, leucine, and methionine are considered to be the most important flavor precursors for generating the flavor compounds of bread (Schieberle 1996). Peptides may be one reason for the bitter perception of rye (Heiniö and others 2012). It cannot be excluded that *fatty acids* may also contribute to flavor formation.

Not all chemical compounds are flavor active, but their odor or flavor thresholds (van Gemert 2003) and relative amounts in the product considerably influence the perceived flavor. For example, many long-chain hydrocarbons do not produce any odor perception. The thresholds are important in the attempt to explain the perceived flavor, though they should always be considered as indicative, qualified, and regarded with some caution.

Odor-active volatile compounds may be related to the perceived odor by GC/olfactometry, by setting odor-active values (OAV) (Grosch and Schieberle 1997), by aroma extract dilution analysis (AEDA) (Schieberle 1996; Grosch and Schieberle 1997). Flavor release can be determined by model mouths and in-mouth techniques. Statistical multivariate techniques, such as PLS regression, and correlation methods are used to link perceived attributes to instrumentally determined chemical compounds (Molteberg and others 1996; Karlsen and others 1999; Zhou and others 2000; Heiniö and others 2001, 2002, 2003b; Martin and others 2002; Noble and Ebeler 2002).

Functional ingredients

Consumption of whole grain foods has, in several epidemiological studies, been shown to reduce the risk of many chronic diseases, such as diabetes, cardiovascular disease, and certain cancers (Jacobs and others 1998; Anderson 2003; Montonen and others 2003; Okarter and Liu 2010). In particular, dietary fiber is considered a primary factor contributing to observed health effects. Grains also have a beneficial composition of fatty acids and proteins, and their high amounts of bioactive compounds have contributed to grain products being deemed exceptionally healthy. Bioactive compounds (phytochemicals), such as lignans, antioxidants, phenolic acids, phytosterols, minerals, tocotrienols, and other vitamins, are mainly concentrated in the germ and in the outer layers of the kernel (Liukkonen and others 2003). Germ also provides lipids, nutrients, phytochemicals, pigments, carotenoids, and anthocyanins.

Dietary guidelines in several countries recommend an increase in the consumption of whole-grain cereals, but in many Western countries consumption is far below the given recommendations. Most varieties of cereal are commonly used when they have been fractionated and not as whole grain. Oat and rye are traditionally consumed as whole grains. The health benefits of oats are especially based on their cholesterol-lowering function, and rye is known for its very high and health-beneficial fiber content in addition to its high content of bioactive phytochemicals. Bran fractions of grain, rich in fiber and health-beneficial phytochemicals, however, often bring problems in processing. Pretreatment, such as extrusion cooking or fermentation of bran, may aid in this.

The whole-grain ideology is constantly growing, and new target groups of consumers might be reached with these products. Product development should recognize consumer needs, and the demand for new types of whole-grain cereal foods among health-conscious consumers does exist. By applying different bioprocessing techniques, the sensory characteristics of cereal – flavor and texture, in particular – may be considerably adjusted. Adjusting cereal flavor and texture to create products that are a rich source of bioactive phytochemicals, nutritionally of good quality, preservable, and particularly palatable should lead to industrial applications in bakery, breakfast, and snack products, but also as a raw material for, for example, the dairy or confectionery industry. According to bakery forecasts, the market for specialty breads in particular, such as multigrain, rye, focaccia, ciabatta, and products with added fiber and functional ingredients, is growing, at least in Europe. A general trend in foods worldwide is to produce low carbohydrate, low calorie, and high fiber products with health benefits. Cereal whole-grain products are well in accord with this trend. In addition to low carbohydrate products, low glycemic index (GI) products are becoming more popular.

Summary

In conclusion, the flavor of cereal is formed as a combination of volatile and phenolic compounds, amino acids and peptides, sugars, and fatty acids, and their relative amounts significantly influence the perceived flavor. The flavor of native grain is mild, but by bioprocessing, such as sourdough fermentation, germination, and enzymatic treatment, or by extrusion or milling fractionation, the cereal flavor can be modified as desired. In addition to containing fiber and bioactive compounds, health-beneficial whole-grain products must also be tasty to be attractive to the consumer.

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23
Nutritional Attributes of Bakery Products

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Introduction

This chapter on the nutritional properties of bread concentrates on the new role of bread as a staple food source that contributes excess calories fueling the obesity epidemic but has also been shown to reduce risk factors for diabetes and cardiovascular disease in epidemiological studies. Recent nutritional research has focused on producing breads that improve physiological and metabolic markers of improved health. The chapter concentrates on bread, the base of many bakery products, since the nutritional properties of other bakery products may be dominated by their fat and sugar content. The basic nutritional composition of breads has not changed appreciably for thousands of years and yeast leavened breads have been consumed for over 6000 years. Bread is truly the "staff of life" for the population of many continents because wheat, the most common grain source for bread, is adaptable to diverse climatic conditions. While it is still the source of healthful energy and protein for many populations, it is also a source of excess calories contributing to the obesity epidemic in many developed and developing countries. Carbohydrates are the major component of wheat and other grains and are a source of caloric energy. Wheat is also the major dietary source of vegetable protein for many people and is higher in protein content than the other two major grains, rice and corn. In addition to the widespread environmental adaptability of bread wheat, the sensorial qualities of bread wheat are due to its unique gas trapping protein, gluten, necessary for good loaf volume. In the past 30 years bread has contributed to the problem of overnutrition and obesity in the United States and other developed countries due to its desirable flavor and low cost. The physiological effects of bread consumption are due both to its composition and processing. In its most basic form bread can be made entirely from only flour, yeast, water and salt. However, bakers have found that removal of selective fractions of the grain during the milling processes and the addition of fat, sweeteners and flavors can increase the culinary opportunities and consumption for bread and other baked goods. In recent years health promoting ingredients such as folate, dietary fiber, beta-glucans, bran, other cereals and seeds, unsaturated fats, organic acids and other ingredients known or regarded as health promoting have been incorporated into breads. The use and nutrition of whole grains have been reviewed recently, for example in the book by Marquart (2007). This chapter will concentrate on recent research concerning the effects of processing and wheat components that alter the physiological response to bread intake and contributes to obesity and metabolic diseases such as diabetes and cardiovascular disease.

Obesity related chronic metabolic disease and food intake

Most recent bread research has focused on its effect on glucose metabolism and obesity because excessive intake of calories over the amount expended through physical activity has resulted in significant growth in the population of overweight (BMI > 25) and obesity (BMI > 30) in the United States and other developed and developing countries. While the US population at 80% is the most visibly overweight and obese, some small countries such as Nauru, Cook Islands, Micronesia, and Tonga are more than 90% overweight or obese (Ono and others 2005) and suggests that obesity of any population with unchecked caloric intake can reach higher levels. Obesity is correlated with increased risks for cardiovascular disease, type 2 diabetes, high blood pressure, and other diseases that shorten life, decrease the quality of life, and increase health care costs for all. Although several epidemiological studies have shown that populations that consume whole grains have lowered risk factors for cardiovascular disease, a recent analysis of whole grain studies points out that many of these studies included oats and that effects on mortality was not reported (Kelly and others 2007). Epidemiological evidence suggests that whole grains are also protective against type 2 diabetes and may also lower serum glucose (Murtaugh and others 2003).

Cereal grains, including bread, have contributed to the increased caloric intake. Between 1970 and 2000, *daily* caloric intake per person in the United States increased by 530 cal (Figure 23.1). Annual wheat flour consumption increased 28% from 52 to 66 kg/person during this period. This increase in cereal grain intake is about 140 cal/day per person assuming 3.5 cal/g for the caloric content of cereal flours. A slice of bread (30 g) contains about 80 cal, 12 g of starch and 2 g of protein. Cereal grains have contributed significantly to the total daily energy increase since 1970. The increased consumption of cereal grains and breads in particularly are due to its low cost, availability, and desirable flavor and textural characteristics. The mild and pleasant flavor of bread makes it an ideal carrier for sauces, meats, cheese, and other fat and sweeteners such as sandwiches, hamburger, pizza, pastries, cakes, and other appetizing but high calorie foods. Higher fat and sugar consumption have also contributed to obesity. The physiology of nutrient utilization does not depend on food composition and preparation alone. The same amount of food fed for two weeks as 17 small meals decreased serum total and low-density lipoprotein (LDL) cholesterol compared or 3 large meals daily (Jenkins and others 1989).
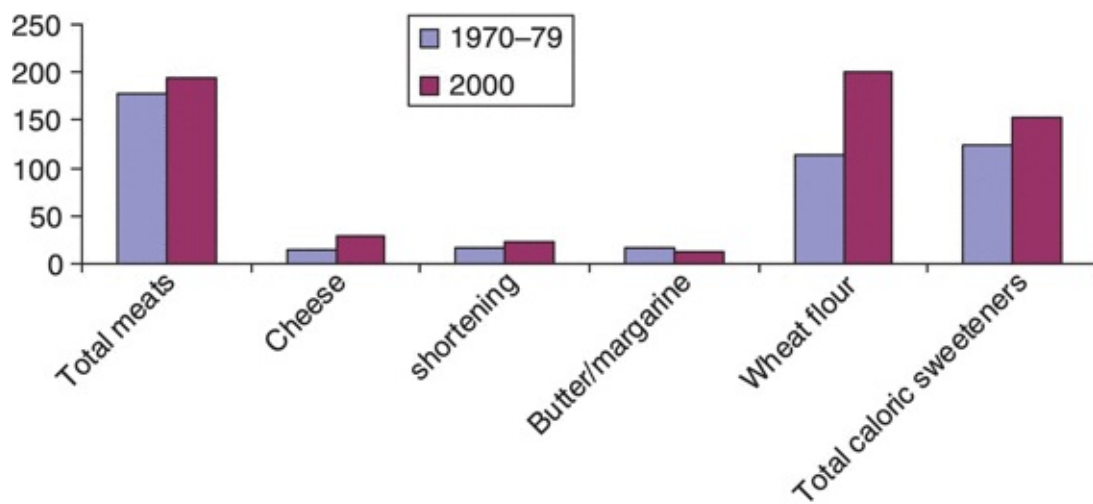
Figure 23.1 Consumption of selected food groups in U.S. (selected data from USDA 2001–2002).

Recent research on the causes of obesity and related chronic diseases have focused on the role of gut bacteria, the microbiota (Harris and others 2012). Colonic bacteria can promote obesity by metabolizing and increasing energy harvest from cereal fibers, resistant starch, and oligosaccharides that are not absorbed in the small intestine and also are the source of chronic inflammation observed in obese individuals. Although early research suggested that the ratio of the phylum Firmicutes to Bacteriodetes were lower in obese mice and humans (Ley and others 2005, 2006) subsequent research by others found either the reverse of these phyla populations or no differences between lean and obese in animals or humans (Jumpertz and others 2011). However, the Firmicutes have been shown to harvest additional caloric energy in germ free mice inoculated with colonic bacteria from obese humans (Turnbaugh and others 2008) and to increase in lean individuals fed higher than normally consumed energy meals and increase energy harvest (Jumpertz and others 2011). Mice fed high-fat (HF) diets, 60% fat energy, supplemented with 10% wheat arabinoxylan (AX) extracts for 4 weeks had decreased weight gain, decreased visceral adipose weight, lowering fasting insulinemia, lower insulin resistance, smaller adipocyte size, lower total cholesterol, and lower liver free cholesterol compared to mice on HF diet alone (Neyrinck and others 2011). Further, the expression of genes for the intestinal barrier proteins, ZO-1 and occludin, were increased by AX supplementation compared to both the HF and standard chow control diets. Serum inflammatory markers, IL-6 and MCP-1, were also decreased by AX feeding compared to HF. Rats fed wheat bran had lower arabinose:xylose ratio in colonic pellets compared to AX in the feed, but similar ratio of arabinose : xylose in the feces compared to the feed (WH Yokoyama, unpublished results). These results suggest that xylose is metabolized in the cecum or in the proximal colon followed by arabinose and consumption of wheat bran improve metabolic disease by modification of intestinal barrier protein and pro-inflammatory cytokines.

Dietary fiber

The total dietary fiber (TDF) content of wheat breads are typically about 2 and 8% for white and whole wheat breads (Prosky and DeVries 1992). Resistant starch present at 1–8% in breads, may also be considered a form of dietary fiber (McCleary 2007), is produced by the bread making process and can be enhanced by processing or by supplementation with high amylose flours. The soluble dietary fiber (SDF) content of both white and wheat breads is about 1%; the remainder being insoluble dietary fiber (IDF). This suggests that the SDF resides mainly in the endosperm. Cellulose (linear glucose polymer) and hemicellulose (branched AX polymer) make up most of the TDF. Hemicellulose is cross-linking by ferulic acid and also bound to lignin. These linkages affect its physicochemical and nutritional properties such as solubility, waterbinding, viscosity, and digestibility. The digestibility of cellulose, hemicellulose, and lignin were found to be 0.2, 0.46, and 0.04, respectively (Van Dokkum and others 1983) in humans who were fed breads with a wide range of TDF content. These results are supported by a fiber recovery study (Silvester and others 1995; Lia and others 1996) in which 72% of the dietary fiber and all of the resistant starch passed undigested through the small intestine in human ileostomy effluents. Some of the undigested cellulose and hemicellulose are fermented by colonic microbes to short chain fatty acids such as acetate, propionate and butyrate.

Dietary cellulose and other fibers, particularly soluble fibers, also increases fat, bile acid (Gallaher and Schneeman 1985), and cholesterol excretion (Kim and others 2011; Yokoyama and others 2011) in animal models. Lipid excretion, decreased blood insulin levels, and short-chain fatty acid fermentation products are hypothesized to be mechanisms (Gunness and Gidley 2010) of plasma cholesterol lowering and/or decreased weight gain. Viscous SDF such as psyllium, cereal β-glucans, guar gum, pectin, xanthan gum, and hydroxypropyl methylcellulose are more effective cholesterol lowering agents than IDF. However, in a study of pigs fitted with portal vein catheters, glucose absorption and starch recovery was decreased by both an insoluble source of fiber (wheat bran) and a fiber that contained significant amounts of soluble fiber (oat bran) compared to the low fiber diet (Bach Knudsen and others 2000). Since recovery of glucose from starch was affected, delayed gastric emptying is not involved. Wheat (Isaksson and others 1982) and other brans contain substances such as polyphenolics (Hargrove and others 2011) that interfere with pancreatic amylase hydrolysis of starch.

Although only trace amounts of β-glucans are found in wheat (Philippe and others 2006), breads with higher soluble fiber content formulated with oat or barley are available in the marketplace. A health claim can be made for reducing risk of heart disease due to β-glucan content if the reference amount customarily consumed (RACC) contains 0.75 g of β-glucan from whole oat or barley. Processing and endogenous glucanases can hydrolyze the glucan polymer, reducing its molecular weight and viscosity (Yokoyama and others 1998). Viscous SDF also reduce the postprandial glycemic response (Jenkins and others 1978). While substantial hydrolysis may not affect the hypocholesterolemic properties of β-glucans, food processes can reduce β-glucan polymer size and their glycemic properties (Regand and others 2009). In a study of the glycemic and insulinemic properties of rye bread and rye bread supplemented with additional β-glucans the glucose response was not different from the control white bread (Juntunen and others 2002). The insulin response was decreased by the

rye bread, but not the rye bread supplemented with β-glucan. The authors suggested that food form and botanical structure may be more important than fiber content.

Resistant starch, like cellulose and AXs, can pass through the small intestine to be partially fermented in the colon. The amount of resistant starch recovered from the ileum is the same as the amount determined in vitro (Silvester et al. 1995). Intact kernels, granules, retrograded amylose, and chemically modified starches are different forms of resistant starch and classified as RS1–RS4, respectively. The resistant starch content of white bread is typically less than 1% (Holm and Bjorck 1992) and is probably mainly RS3.

Starch and glycemic index

The available carbohydrate – starch and sugar – content of bread is about 85%. Starch is a glucose polymer that is hydrolyzed by pancreatic enzymes into glucose. The porosity of bread creates a large surface area for enzymatic hydrolysis and as a result leavened breads are rapidly digested and have a high glycemic index (Wolever and others 1985; Foster-Powell and others 2002; Atkinson and others 2008). The absorption of glucose stimulates the pancreas to secrete insulin into the bloodstream resulting in the transport of glucose into liver, muscle, and fat cells to be stored as glycogen. The rate of digestion and absorption depends on many compositional and processing factors including the degree of gelatinization of starch, amylose content (van Amelsvoort and Weststrate 1992; Behall and others 2006), dietary fiber (Holm and Bjorck 1992), fat content, delay in gastric emptying by organic acids (Darwiche and others 2001), food form (Holm and Bjorck 1992), amylase inhibitors, and other factors. The glycemic index, a measure of the postprandial rise and decline of blood glucose after consuming different carbohydrate containing foods, was developed by Jenkins and coworkers (1981) to put a number on the rate of absorption of glucose from carbohydrate foods. It is recognized as useful and is widely used, but GI for a particular food can vary widely depending on the biological variability of plant foods, processing, and methodology. Postprandial insulin level also rises and falls and the corresponding insulinemic index has been defined. Excessive caloric intake, including carbohydrates and fat, results in obesity and insulin resistance. The transport of glucose from the blood into peripheral tissues – muscle and adipose – requires insulin. With insulin resistance higher blood levels of insulin are required to dispose of glucose. High fasting blood glucose (FBG) has been shown to be a predictor of increased risk of type 2 diabetes (Brambilla and others 2011). High FBG is often accompanied by insulin resistance.

Ferulic acid and other cereal phenolics

Wheat contains significant amounts of ferulic and other phenolic acids, mainly in the bran ([Figure 23.2](#)) (Adom and others 2005). Free phenolic acids are perceived as bitter and removal of the bran reduces this flavor attribute. Human subjects fed 10.2 mg/d of ferulic acid excreted 4.8 mg/d in the urine showing that ferulic acid is bioavailable (Harder and others 2004) but ferulic acid intake did not affect LDL oxidation in vitro. Ferulic and other phenolic acids are mainly absorbed in the colon (Poquet and others 2008) and have been linked to anticancer activities (Janicke and others 2011). Ferulic acid and resveratrol have been shown to reduce the proinflammatory marker NF-kB in the alloxan-treated mouse diabetes model (Ramar and others 2012).
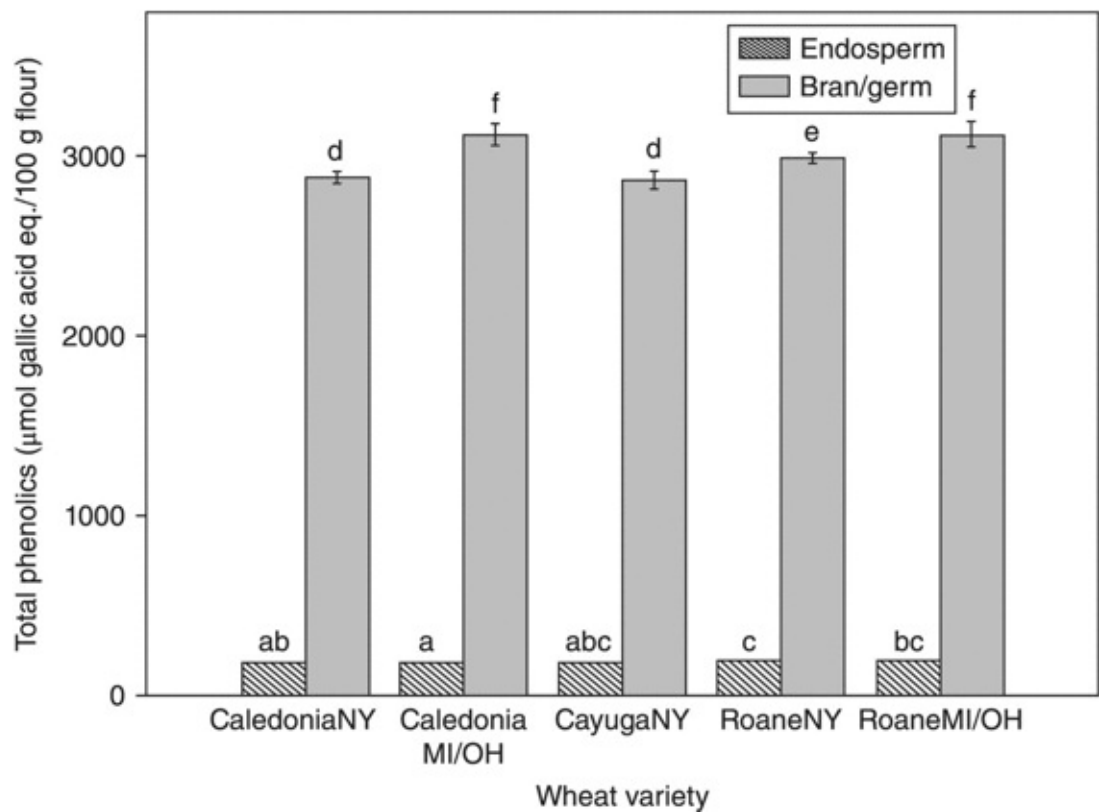
Figure 23.2 Total phenolic content of milled fractions of wheat varieties. Data represent mean ± SD ($n = 3$). Bars with no letters in common are significantly different ($p < 0.05$) (Adom and others 2005).

Summary

The constituents of bran have been shown to produce physiological effects that reduce the risk factors for diabetes, cardiovascular disease, and other metabolic diseases related to obesity. Recent research and development has focused on the role of fiber including resistant starch to decrease the glycemic response, increase short chain acid production, and improve intestinal barrier function. The importance of the colonizing intestinal bacteria, the microbiota, and the fermentation of fiber and associated phenolic acids are a new area of bread-related health research.

Acknowledgments

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24

Browning in Bakery Products: An Engineering Perspective

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Introduction

Bakery products have typical quality features that are diverse and depend on the particular product and its country or region of origin (for example, there are regional variations of the same product). Surface color is an important sensory attribute particularly associated with appearance, aroma, taste, and with the overall quality of bakery products. It has a significant effect on consumer judgment as color influences the anticipated oral and olfactory sensations because of the memory of previous eating experiences (Abdullah 2008). Therefore, surface color plays a key role in the acceptance of the product by consumers, and it is often used to determine the end point of the baking process.

The formation of color in bakery products occurs during the baking stage (unless colored ingredients or colorants are being used, which not within the scope of the present discussion). This phenomenon is widely known as browning and is the result of non-enzymatic chemical reactions that produce colored compounds during baking, such as the Maillard reaction and caramelization. The Maillard reaction takes place where reducing sugars and amino acids, proteins, and/or other nitrogen-containing compounds are heated together, while caramelization describes a complex group of reactions that occur when carbohydrates, particularly sucrose and reducing sugars, are heated directly (Fennema 1996). Because of the type of reactants and products involved in the Maillard reaction and caramelization, the importance of browning development is not only related to sensory aspects but also to nutritional properties. For example, the Maillard reaction impairs the content and bioavailability of amino acids and proteins, and is related to the formation of harmful compounds such as acrylamide and hydroxymethylfurfural (HMF). However, some reaction products are associated with positive nutritional properties such as antioxidant activity.

Like other chemical and physical changes, browning depends on temperature, water activity (the amount of water available for reactions), and pH of the food. From an engineering perspective, this dependence is established through transport phenomena that occur during baking. Basically, heat and mass transfer determine the variations in temperature and moisture content (and thus water activity) of food, which is actually a non-ideal system under dynamic conditions (pH is determined by product formulation). Although this approach is complex, it is appropriate for food engineers and technologists. The (classical) chemical viewpoint is fundamental since it aims to establish the reaction pathways and the dependence on experimental conditions. An engineering approach, however, is necessary for industrial applications to extend basic knowledge to real systems and processes.

As the development of color in bakery products is of importance, this chapter reviews the browning phenomenon with emphasis on engineering aspects. This perspective of browning includes basic concepts for understanding the chemistry of reactions, the consequences for product quality, and process design topics, such as measurement, modeling, control, and optimization based on the fundamental concepts of transport phenomena that occur during baking. Note that the discussion is focused on general bakery products, that is, those obtained from basic dough formulated mainly with flour and water, and additionally sugars.

Basic concepts of browning

Considering the objective and perspective established for this chapter, only fundamental concepts of chemistry of browning reactions will be discussed, with the aim of giving an adequate background to understand the development of color during the baking process and its consequences on the quality of bakery products. For a detailed discussion about this topic, the reader is referred to basic literature (Hodge 1953; Baltes 1982; Kroh 1994; Namiki 1988; Fennema 1996; Martins and others 2001). Essentially, the development of browning in bakery products is the result of the Maillard reaction and caramelization. Ingredients of bread, cake, and biscuit (carbohydrates, proteins, and water), are actually the reactants for these chemical reactions, which are catalyzed by a low to medium moisture level and the high temperature attained at the product surface during baking.

The Maillard reaction is a complex network of reactions involving reactants and products with high reactivity, and its mechanism is still a controversial issue, so the reaction is difficult to control. In general terms, the reaction starts with a condensation between a reducing sugar, such as glucose, and a compound that has a free amino group of an amino acid or, mainly, the ε-amino group of lysine in proteins. The condensation product (N-substituted glycosylamine) is then rearranged to form the Amadori product (1-amino-1-deoxy-2-ketose), which is subsequently degraded into different compounds depending on the pH of the system. At low to medium pH (4–7), HMF or furfural (when hexoses or pentoses are involved, respectively) are formed via enolization. These highly reactive compounds take part in further reactions of condensation and polymerization to form melanoidins and other insoluble brown polymers, and aromatic substances (Martins and others 2001). A simplified scheme of the Maillard reaction is shown in Figure 24.1, where only the pathway corresponding to the formation of color via HMF or furfural is depicted. This is the route commonly associated with browning development in bakery products because of the pH range, and experimentally followed by HMF quantification. Other reaction pathways (pH > 7) involve sugar dehydration and fragmentation, amino acid degradation (Strecker degradation), and eventually polymerization and formation of melanoidins (Hodge 1953). It is worth mentioning here that when certain amino acids (for example, asparagine) are involved in the Maillard reaction, the potential cancer-causing agent acrylamide can be generated. Because the formation of acrylamide is favored by high temperatures, and acidic and neutral pH conditions, this issue is of great concern to the baking industry (Mottram and others 2002; Stadler and others 2002).
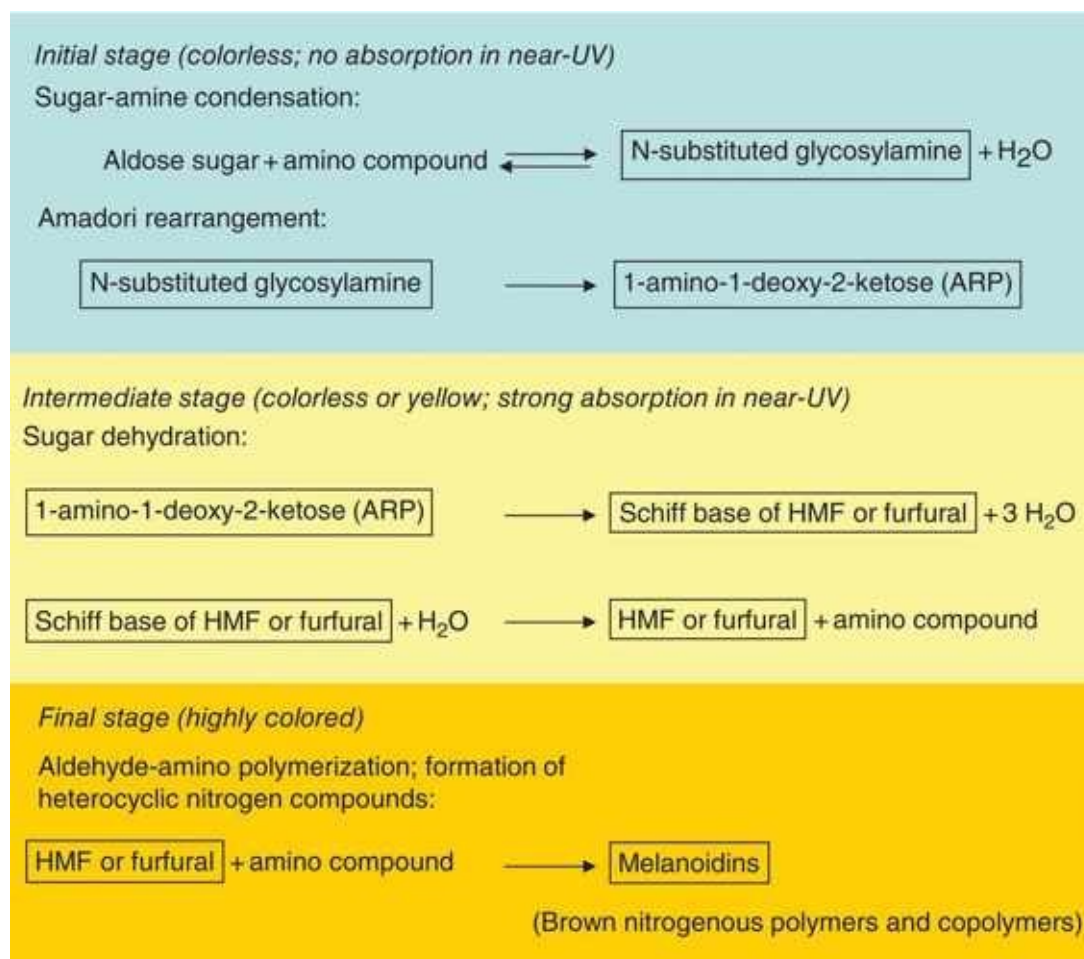
Figure 24.1 Simplified scheme of the Maillard reaction (pH < 7). ARP, Amadori rearrangement product; HMF, hydroxylmethylfurfural. (Purlis 2010).

Caramelization is also a complex group of reactions initiated by heating of carbohydrates, in particular sucrose and reducing sugars, without nitrogen-containing compounds (Fennema 1996). Kroh (1994) described a principal sequence of sugar degradation reactions as follows: initial enolization, dehydration, dicarbonyl cleavage, retro aldolization, aldolization, and finally, radical reaction. The key intermediates of this series of reactions are the osuloses (α-dicarbonyl compounds) obtained after enolization and dehydration, which lead to the formation of products with double bonds or unsaturated rings such as derivatives of furan, for example, HMF, and polymers (after condensation). Caramelization is catalyzed by acidic conditions and the presence of certain salts (such as ammonium salts). During baking, starch and sucrose can be hydrolyzed leading to reducing sugars that can participate in both types of browning reaction, so the Maillard reaction and caramelization may take place simultaneously in bakery products (Capuano and others 2008).

The consequences of browning reactions involving reactants, intermediates, and products is analyzed in the following section in the context of baking bakery products.

Browning during baking

Before discussing the occurrence and effects of the browning reactions in bakery products, let us consider the baking process to give an adequate context for the real system and conditions where the Maillard reaction and caramelization take place. Basically, baking consists of a simultaneous heat and mass transfer process between the product and the oven ambient. At the beginning of the process, raw dough with uniform temperature and water content is placed in the oven at high temperature (> 150 °C) and low relative humidity (note that vapor injection can be used in some applications). Consequently, the temperature at the food surface rises, increasing the water vapor pressure and thus establishing the driving force for drying. When the temperature reaches about 100 °C, an evaporation front is formed where water evaporation takes place. Once the product has been dehydrated locally, the evaporation front advances towards the core, generating a dry crust typical in bread and similar products (Lostie and others 2002a, 2002b, 2004; Purlis and Salvadori 2009a, 2009b). In this outer zone, the water content decreases to 5–10% (wet basis; these values correspond to bread), while the temperature rapidly increases above 100 °C, tending to the oven temperature asymptotically. These variations in temperature and moisture content give certain structural characteristics to the crust that avoid dehydration of the inner regions by limiting the water vapor migration to the oven ambient. In fact, the inner zone of products, the crumb, does not dehydrate and temperature increases asymptotically to the evaporation front temperature. It is worth noting that thin products such as biscuit may present different internal mechanisms of heat and mass transport, thus showing different moisture and temperature profiles; however, similar changes occur at the surface giving the same general characteristics of browning development (Ait Ameur and others 2007; Gökmen and others 2008a). In summary, two different regions can be distinguished in bakery products such as bread and cake: the crumb, which is the inner zone where the temperature does not exceed 100 °C and dehydration does not occur; and the crust, which is the outer zone where the temperature surpasses 100 °C and dehydration occurs. Thin products can be considered as a single zone with characteristics similar to crust.

It can be seen that during the baking process, dynamic conditions are generated where temperature and water content (and activity) change continuously and in a non-straightforward way in the product. In this sense, browning reactions take place in a non-ideal system where temperature and water activity cannot be controlled as in an ideal experiment, and reactants are provided by product formulation. In this context, we will analyze the development of browning and its consequences on the overall quality of bakery products.

Sensory quality aspects

Browning has been already defined as the phenomenon that generates the typical color of bakery products, but it also plays a key role in the formation of compounds related to aroma and taste (or flavor). In this sense, browning reactions affect other main sensory attributes besides texture.

The development of color is a dynamic process that depends on transport phenomena that occur during baking, and results from the production and accumulation of colored

compounds via the Maillard reaction and caramelization, that is principally HMF and melanoidins. Then, browning can be followed by measuring the concentration of reaction products or alternatively, the degree of reactants consumption; this is a chemical way of monitoring browning. On the other hand, the concept of lightness is commonly used to describe the variation of color during baking. Lightness (L^*) is a coordinate of the CIE $L^*a^*b^*$ color space, which is an international standard for color measurement widely used in food science and technology; L^* ranges from 100 (black) to 0 (white) (Yam and Papadakis 2004). Typical lightness values of raw dough are between 80 and 95 (Shibukawa and others 1989; Purlis and Salvadori 2009c; Ramírez-Jiménez and others 2000b), although lower values can be registered depending on dough formulation, e.g. aggregate of egg or high amount of sugar leads to a darker dough (Broyart and others 1998). From the chemical viewpoint, HMF cannot be detected in raw dough since it is a product of browning (non-enzymatic) reactions and therefore it is not present in unbaked foods (Ait Ameur and others 2006).

During the baking process, one or two stages can be distinguished in the variation of product lightness. The first stage is characterized by a lightening of the surface and corresponds to the first minutes of baking. This phenomenon is not logical since it is against browning chemistry; however, it has been reported by some authors. In biscuit baking, Shibukawa and others (1989) measured a slight increase of lightness (about 2.7%) at the early stage of heating (first 5–10 min) and suggested the drying of the surface to be responsible. Broyart and others (1998) also observed this phenomenon (a lightness increase between 7.9 and 11.8%) during cracker baking and suggested that the initial increase of product thickness (cracker spring) to explain it. A similar hypothesis was proposed by Purlis and Salvadori (2007, 2009c), who observed 1.2–3.5% increase of surface lightness in bread after 5 min baking. Probably, this first stage of lightning is due to physical changes occurring at the product surface at the beginning of the process. After proving and before baking, the surface of raw dough is wrinkled, irregular, but after a few minutes of heating, it becomes considerably smoother due to an increase in volume. This change in surface texture may be the reason for the observed initial lightening, since a smooth regular surface can reflect more light than a wrinkled irregular one. Therefore, this first stage is only related to the method used for measuring browning development, that is, reflectance or visual techniques using a colorimeter or a computer vision system. From a chemical point of view, this first stage is a lag phase where the food system conditions (temperature and water activity) do not allow the formation of colored compounds by browning reactions.

The second stage is the formation of color or surface darkening. In general, browning is detected when the water activity decreases to 0.4–0.7 and the temperature surpasses 105–120 °C (Table 24.1). The previous description of the baking process from the transport phenomena viewpoint, indicates that only the surface (or crust) of bakery products can show a significant change in color. For instance, HMF is detected almost exclusively in the crust of bread samples (Ramírez-Jiménez and others 2000b; Capuano and others 2008). The minimum temperature and water activity requirements are related to the pyrolytic conditions needed for browning reactions, that is, a high temperature and a low water activity obtained via dehydration. Table 24.2 is included to give a general reference of typical values of HMF and/or L^* in bakery products obtained by conventional baking.

Table 24.1 Temperature and water activity values for initiation of browning for different bakery products (Purlis 2010. Reproduced with permission of Elsevier).

Product	Temperature (°C)	Water activity	Reference/observations
Biscuit 100% flour 50% sugar 20% margarine ~20% milk 5% eggs	> 120		Shibukawa and others (1989) L^* determination
Biscuit 100% flour 37% sugars 17.5% water 16% fats	> 105–115		Broyart and others (1998) L^* determination
Biscuit 100% flour 50% sugar syrup 17% palm fat		< 0.4–0.7	Ait Ameur and others (2006, 2007) HMF determination
Biscuit 100% flour 44% sugars 40% shortening 22% water 1.5% leavening agents 1.25% salt		< 0.4	Gökmen and others (2008b) HMF determination
Bun 100% flour ~57% skimmed milk 11.4% margarine 9.7% sugar 5.7% fresh yeast	> 110		Wählby and Skjöldebrand (2002) L^* determination
Bread 100% flour 54.1% water 1.6% salt 1.6% sugar 1.6% margarine 1.2% dry yeast	> 120	< 0.6	Purlis and Salvadori (2009c)L^* determination

Table 24.2 Some typical values of lightness (L^*) and HMF concentration (mg/kg dry matter) in bakery products for various baking conditions. Ranges of L^*, HMF and/or operating conditions are ordered respectively (Purlis 2010. Reproduced with permission of Elsevier).

Product	L^* or HMF	Operating conditions	Reference
Biscuit	$L^* = 40$–50	19 min, 200 ºC	Shibukawa and others (1989)
	$L^* = 55.7$–14.4	6 min, 240–330 ºC	Broyart and others (1998)
	$L^* = 57.$	90 min, 180 ºC	Ramírez-Jiménez and others (2000a)
	HMF = 15.6		
	HMF = 0.49–74.6	(Commercial, unknown)	Ait Ameur and others (2006)
Fermented dough, ~10% sucrose	$L^* = 65.6$	8–10 min, 220 ºC	Ramírez-Jiménez and others (2000a)
	HMF = 151.2		
White bread	$L^* = 84.1, 77.2$	50 min, 200 ºC	Ramírez-Jiménez and others (2000b)
	HMF = 11.8, 68.8		
	$L^* = 81.6$	60 min, 200 ºC	
	HMF = 40.1		
	$L^* = 81.9, 82.1$	30 min, 210 ºC	
	HMF = 3.4, 15.7		
	$L^* = 83.0$	16 min, 235 ºC	
	HMF = 21.8		
Bread crisp	$L^* = 80.73$	40 min, 140 ºC	Capuano and others (2008)
	HMF = 2.53		
	$L^* = 72.40$	34 min, 160 ºC	
	HMF = 14.63		
	$L^* = 63.48$	25 min, 180 ºC	
	HMF = 47.02		
Bun	$L^* = 52.13$	8 min, 225 ºC	Esteller and others (2006)
Muffin	$L^* = 83.9 \pm 2.8$	(Commercial, unknown)	González-Mateo and others (2009)

Dough formulation is also relevant for browning development because it provides the reactants for the Maillard reaction and caramelization. In bakery products, the content and type of sugar are the main variables affecting color formation (glazing and topping will not be discussed for sake of generalization). In general, HMF formation increases with sugar content, but depending on baking conditions, sugar degradation may proceed in different ways. For instance, at oven temperatures below 300 °C, sucrose is stable, and glucose and fructose produce more HMF (Ait Ameur and others 2007; Gökmen and others 2007). Conversely, for greater heating conditions, sucrose can be totally hydrolyzed and the derived fructose and glucose appear more reactive in producing HMF than pre-existing hexose in products formulated with glucose and fructose. Also, fructose can generate more HMF than glucose in any baking condition (Ait Ameur and others 2007). Another important ingredient is the type of (chemical) leavening agent; the use of ammonium bicarbonate reduces the pH of dough, thus accelerating the degradation of sucrose and consequently the formation of HMF during baking (Gökmen and others 2008b).

However, when temperature is high and low water activity is achieved at the product surface by intensive baking conditions or by prolonged processing times, sugar caramelization takes place producing more colored compounds in addition to the Maillard reaction products. This drastic condition is responsible for a burnt appearance characterized by low product lightness . For bread, this situation can be represented by lightness values lower than 60 (Purlis and Salvadori 2009c).

Browning reactions also produce compounds that contribute to aroma and taste or to the flavor attributes of bakery products which are essential for the initial judgment of consumers. In the Maillard reaction, the type of flavor compound generated depends on the type of sugars and amino acids involved, while temperature, time, pH, and water content of the system influence the reaction kinetics (Martins and others 2001; van Boekel 2006). Decarboxylation and deamination of amino acids by dicarbonyl compounds (Strecker degradation) lead to the formation of aldehydes; this mechanism is of major importance to flavor generation via the Maillard reaction, though other pathways are also possible (van Boekel 2006). The degradation of sugars in the absence of amino acids (caramelization) also gives typical flavor compounds, especially related to caramel aroma (Kroh 1994; Fennema 1996). Some typical and thus desired compounds associated with the flavor of bakery products are 2-acetyl-1-pyrroline, 4-hydroxy-2,5-dimethyl-3(2H)-furanone, methional, methylpropanal, 2,3-butanedione, maltol, and isomaltol (Fennema 1996; Rychlik and Grosch 1996; Vanin and others 2009).

Nutritional aspects

The development of browning also produces important effects on the nutritional properties of bakery products. At the beginning of the Maillard reaction, the condensation between reducing sugars and amino acids destroys the amino acids involved, as well as forming melanoidins at the final stage (see [Figure 24.1](#)). This is particularly important for lysine, an essential amino acid whose ε-amino group is the major source of primary amines in proteins; lysine is no longer biologically available before color is noticeable (Fennema 1996). Furthermore, during browning, oxidation and destruction of other essential amino acids (e.g. methionine and tryptophan) and cross-linking of proteins (also related to formation and setting of crust) occur, thus impairing the digestibility of the proteins involved and reducing

the nutritional quality of bakery products (Morales and others 2007).

The Maillard reaction is also associated with the formation of acrylamide, a potentially carcinogenic compound (Mottram and others 2002; Stadler and others 2002). In 2002, significant amounts of acrylamide (150–4000 µg/kg) were found during cooking of carbohydrate-rich foods (Tareke and others 2002). Bakery products, together with potato products and coffee are the most important sources of acrylamide (Claus and others 2008). because of the high concentration of asparagine in the raw materials of these products, which is crucial in the formation of acrylamide by the Maillard reaction. For instance, the asparagine concentration in wheat flour is 167 mg/kg, corresponding to 14% of the total free amino acids (Mottram and others 2002). It is worth noting that the same pathway (Strecker degradation) that generates the desired flavor compounds can also produce acrylamide if asparagine is present (Stadler and others 2002). The reported values for acrylamide concentration in bread crust range between 85 and 230 µg/kg, for conventional baking at 200–270 °C for 10–20 min (Surdyk and others 2004; Ahrné and others 2007); for biscuits, acrylamide concentration ranges between 150 and 229 µg/kg (Gökmen and others 2008a).

The production of acrylamide is strongly correlated with baking temperature and time, and the amount of asparagine and reducing sugars present; the reaction starts at 120–130 °C (a range similar to color formation), so it can be only found in the crust of bakery products (Becalski and others 2003; Surdyk and others 2004; Bråthen and Knutsen 2005; Ahrné and others 2007). In conclusion, acrylamide formation is highly correlated with color development since it is produced mainly by the same group of reactions during baking. This represents a major challenge for food engineers: the same reactions that produce the desired color and flavor also generate toxic compounds. Therefore, mitigation strategies have been proposed to reduce the concentration of acrylamide during baking: use of sucrose instead of reducing sugars (Gökmen and others 2007); use of sodium hydrogencarbonate instead of ammonium hydrogencarbonate as leavening agent (Amrein and others 2004; Graf and others 2006); addition of asparaginase (Capuano and others 2008); and steam and falling temperature baking (Ahrné and others 2007). However, HMF (a product of the Maillard reaction) is also suspected to be a harmful compound, so its concentration should also be reduced in bakery products (Gökmen and others 2008b).

On a positive note, some products of browning reactions are health promoting substances; for example, reductones and melanoidins present antioxidative activity based on reducing power and metal chelating capability (Baltes 1982; Fennema 1996; González-Mateo and others 2009; Morales and others 2009). Also, desmutagenic effects have been reported in the Maillard reaction (Martins and others 2001).

Engineering aspects of browning

The ultimate goal for food technologists is to predict and control browning development during the baking process, since it affects the overall quality of bakery products, including their sensory and nutritional properties. For this aim, the advance of browning reactions needs to be measured and mathematical models developed describing the process during baking. Afterwards, control, optimization, and design of a baking process can be performed by coupling transport phenomena with browning development to produce safe, high-quality bakery products, as well as fulfilling conventional economic objectives. This section presents the methods and concepts for achieving the established ultimate goal, with a focus on engineering aspects of the baking process.

Measurement

The first step in predicting and controlling the development of browning (or any other change) is its quantification. Experimental techniques can be classified into two categories: chemical (or objective) and sensory (or subjective). The first group measures the concentration of products or alternatively the consumption of reactants of browning reactions; the second group aims to quantify the variation of color. Chemical techniques are mostly intended to measure the concentration of HMF and furfurals in food during baking. The general procedure consists of an extraction method with subsequent quantification by HPLC-UV; UV detection is carried out at 280 or 284 nm (Ait Ameur and others 2006, 2007). A similar protocol is used for determination of furosine, a compound formed during the early stages of the Maillard reaction (Ramírez-Jiménez and others 2000b). The advance of browning reactions can also be followed by measuring the consumption of reactants. For instance, the degradation of sugars can be quantified with a HPLC-RI (refractive index) detection method, after a water-ethanol extraction (Ait Ameur and others 2007).

Sensory methods are based on a technological approach by monitoring the changes in color of products, with no direct reference to chemical reactions. Basically, this type of techniques quantifies the amount of light reflected by the surface of the food – a reflectance measurement – and results are given in a certain color space. In food science, color is mostly represented by the *Commission Internationale de l'Eclairage* (CIE) $L^*a^*b^*$ color space, which is an international standard for color measurement adopted by CIE in 1976 (León and others 2006). The three variables or coordinates of this model represent the lightness of color (L^*), its position between red and green (a^*), and its position between yellow and blue (b^*) (Yam and Papadakis 2004). The CIE $L^*a^*b^*$ color system is based on the spectral sensitivity of human sight and its adaptation to prevailing lighting conditions (Mendoza and others 2007). Using this concept, different devices have been designed to measure color variation in food products. Conventional equipment includes the colorimeter and similar color sensors, which are specific devices made by different specialized companies, and which can also determine diverse geometry features depending on each particular product or application. Alternatively, the computer vision system is a powerful tool that can be tailor made; it consists of an image acquisition device connected to a computer that processes image data using algorithms. Depending on the acquisition conditions and implemented algorithms, color and geometry features can be determined, and more complex applications such as fuzzy control or pattern

recognition can be carried out (Sun 2008).

Both chemical and sensory methods have advantages and drawbacks. Chemical techniques provide objective data and sensibility, which are important aspects for modeling the browning reactions. These methods are destructive, laborious, and time-consuming, however, so industrial applications are limited. On the other hand, sensory methods are rapid, non-destructive, can be automated, and have a low cost. The type of information provided by sensory methods depends on the final objective. If a chemical-based or mechanistic model has to be developed to describe color formation, these methods are not adequate, unless a calibration curve is available to convert color values into the concentration of a given compound. Nevertheless, subjective data play a key role in the production of bakery products, since they can be directly associated with consumer preference.

Modeling

The development of a mathematical model of browning is essential to predict and then control this phenomenon during baking, as a function of operating conditions and product formulation. The best modeling approach would be a mechanistic one, describing the pathways of the Maillard reaction and caramelization that generate compounds related to color, taste, aroma, and also nutritional aspects. However, browning reactions involve complex mechanisms that are still not well elucidated. In addition, modeling of transport phenomena occurring in bakery goods during baking is also complicated, so temperature and water activity variations are not usually available either. Therefore, modeling of browning development represents a major challenge for food engineers and technologists.

A practical solution to this problem has been the kinetic modeling approach, based on rate constants and activation energies. These kinetic parameters depend on system conditions (such as temperature and water activity), but not generally on composition, so extrapolation of the obtained results is limited. However, kinetic modeling results very useful for many applications that involve quality changes in food processing, because it is based only on the rate-determining steps of a given reaction, and thus provides control points (Martins and others 2001). Therefore, color formation is usually simplified by assuming a general mechanism of browning including both the Maillard reaction and caramelization, described by certain kinetic parameters. Alternatively, the variable representing color change is selected depending on the quantification technique or the final objective of the prediction. For instance, surface lightness measured by a colorimeter or the computer vision system will give sensory information. It is worth noting that these models are empirical and thus will depend on experimental aspects. It is important to analyze the experimental set-up used to obtain the kinetic parameters and validate the model.

Some efforts have been made to predict the development of browning during baking using the concepts of kinetic modeling. For bread, Zanoni and others (1995) proposed a first-order kinetic model for total color difference (this value is the resultant of all coordinates of a given color model), and the reaction rate constant was found to be temperature dependent following the Arrhenius' equation. The model was set up using ground, dried bread crumb as a model system for crust, and heating at a constant temperature with a refractory plate. The authors concluded that kinetic parameters obtained from isothermal experiments cannot be used for practical baking conditions, and also remarked on the influence of water content on browning kinetics. Considering these conclusions, Purlis and Salvadori (2009c) proposed a

first-order kinetic model but with parameters depending on the local temperature and water activity of bread. This model was based on a non-isothermal kinetic approach, since heating and drying and thus browning of bread surface are non-isothermal processes. Kinetic parameters were obtained by using experimental data of lightness during real baking experiments, and numerical simulation of a transport model to describe the variation of temperature and water activity in bread surface.

For biscuit baking, Broyart and others (1998) developed a first-order kinetic model to predict the variation of lightness during the process. For parameter estimation and model validation, baking experiments were carried out at 180–330 °C oven temperature, and color was measured by a reflectance method. In addition, average values of the temperature and water content of the samples were registered in each baking test and included in the kinetic model. The authors emphasized the model had limitations due to the use of average parameters to predict a surface property. Using a chemical method, Ait Ameur and others (2006, 2007) showed that formation of HMF in biscuit follows first-order kinetics as color development, and that water activity highly influences the production of colored compounds.

So far, the development of browning during baking can be well described by a first-order kinetic model, with parameters depending on the local temperature and water activity of the product. In addition, although color formation is caused by a group of complex chemical reactions, the problem can be simplified by assuming a general mechanism of browning, and followed by using color models related to reflectance methods, for technological purposes. Finally, kinetic parameters should be estimated from experiments close to the actual baking conditions – that is a non-isothermal process occurring in a non-ideal system – to obtain better predictions (Dolan 2003).

It is worth mentioning an alternative approach with less (or no) formalism, which is the development of ad-hoc correlations between color values and baking conditions. For example, Purlis and Salvadori (2007) reported an expression for color development during bread baking as a function of product weight loss and baking temperature. This approach is fully empirical with no possible extrapolation of results except for general behavior; it represents a specific practical solution. However, it can help to develop a first and simple tool for prediction instead of depending on experience or visual assessment.

Control, optimization, and design

Because browning affects the sensory attributes and nutritional properties of bakery products, and depends on transport phenomena occurring during baking, it is important to understand, measure, and predict this phenomenon in order to improve the control, optimization, and design of a process. Some engineering applications are reviewed here with the common premise of performing an integral study of the baking process by coupling browning and transport phenomena.

Fuzzy logic and artificial neural networks present interesting tools for food process control based on browning development, because the reasoning and linguistic terms of operators, experts, and consumers can be taken into account (Perrot and others 2006; Allais and others 2007). For bread baking, Kim and Cho (1997) developed neural networks models and a fuzzy controller to reduce the cost of heating the oven and to perform an intelligent control of the process. For biscuit baking, Perrot and others (1996, 2000) applied fuzzy methods for real-

time quality evaluation and feedback control of the process. Another contribution to the field was made by Ioannou and others (2004a, 2004b): they presented a browning process control system that gives the operator a diagnosis of the state of the product/process and proposes actions on process parameters based on a decision model.

Another useful application is the control and minimization of the formation of toxic compounds during browning, for example acrylamide. This is because color development is highly correlated with acrylamide formation (Ahrné and others 2007; Gökmen and others 2008a), and monitoring color changes is easier than quantifying the accumulation of chemical products. For instance, by combining a correlation or calibration curve between color values and acrylamide concentration, with a computer vision system, a process control tool could be developed for both safety and quality evaluation purposes.

Browning development is commonly used to assess the advance of baking and therefore to establish the end point of the process based on sensory parameters. This is because it can be easily monitored during the process by means of in-line sensors, and in a non-destructive way. Consequently, browning has been incorporated in the optimization and design of the baking process (Hadiyanto and others 2008, 2009). Nevertheless, some considerations have to be taken into account when color of bakery products is used to evaluate the end point of baking. For instance, it is possible to not achieve a complete baking due to an incomplete starch gelatinization in products, which actually determines the transition from dough to crumb. This situation occurs when slightly browned products are sought and intense heating is applied, because surface browning is developed at higher rate than starch gelatinization at the product centre. To overcome this problem, a minimum value of 96 ºC at the product centre (or coldest point) has been proposed as a practical solution (Purlis 2011, 2012).

Conclusion

The development of browning in bakery products during baking is a subject of major interest for food engineers and technologists. Browning reactions are responsible for the formation of color, taste, and aroma, and also for the generation of toxic compounds and the diminution of nutritional quality of products. Therefore, the same pathways can produce desired and undesired substances. For a better understanding and thus control of browning, it is essential to quantify and model its development during baking. For these aims, different methods have been developed; a variety of techniques are available for technological applications regarding bakery products. Thus, we should take advantage of the fact that browning is correlated with several quality changes and incorporate the development of color in the control, optimization, and design of the baking process.

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Functional Bakery Products: An Overview and Future Perspectives

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Functional bakery products

Advances in understanding the relationship between nutrition and health, often at the molecular level, have led to the concept of functional foods (also known as nutraceutical or pharmaceutical foods) (Mollet and Rowland 2002; Siró and others, 2008). Today's foods are designed not only to satisfy hunger and provide the necessary nutrients for human beings, but also to prevent nutrition-related diseases and improve the physical and mental well-being of the consumers (Milner, 1999, Hasler, 2002; Siró and others, 2008).

The concept that food intake may be beneficial to health is very old and started 2500 years ago with Hippocrates when he declared "Let food be thy medicine and medicine be thy food." (Milner 1999; Hasler 2002; Bento 2008; Monteiro and Marin 2010).

The first use of the term "functional food" was in Japan in the 1980s, to describe food products fortified with special components that had beneficial physiological effects (Bento, 2008; Siró and others, 2008; Monteiro and Marin, 2010). Functional foods (prebiotic and probiotic foods) can improve the body's general conditions, reduce the risk of certain diseases, and can even be used to cure certain diseases (Hasler 2002; Bento 2008; Siró and others 2008; ADA 2009; Monteiro and Marin 2010). Functional foods do not possess a widely accepted definition (Hasler 2002; Bento 2008; Siró and others 2008; ADA 2009). All foods are functional to some extent, since they provide nutritional value, aroma, and flavor. It is assumed, however, that a food is deemed functional if it originates a beneficial physiological effect to health, specifically a reduction of the risk of developing diseases or for optimizing one's health, in addition to its basic nutritional function (Hasler 2002; Bento, 2008; ADA 2009).

The concept of functional food was promoted in 1984 by Japanese scientists who studied the relationship between sensory satisfaction, fortification, and the modulation of physiological systems. In 1991, the Ministry of Health of Japan introduced rules for the approval of a specific category of health-related foods called FOSHU ("Foods for Specified Health Use"), which included the establishment of specific health claims for this type of food (Hasler 2002; Bento 2008; Siró and others 2008). By July 2002, the status of FOSHU had already been granted to about 300 food products in Japan (Hasler 2002).

Japan published a law as early as June 1997 regulating functional products/health claims in foods. Nowadays, several other countries, including those in the European Community (EC), have specific legislation about the health claims and labeling of functional foods (Monteiro and Marin 2010). In the United States, there are no regulations for functional foods. Several organizations have, however, proposed definitions for this category of food. In 1994, functional foods were defined by the National Academy of Sciences' Food and Nutrition Board as "any modified food or food ingredient that may provide a health benefit beyond the traditional nutrients it contains" (Thomas and Earl 1994; Milner 1999; Hasler 2002). The International Life Sciences Institute defines functional foods as "foods which, due to the presence of physiologically active components, provide health benefits beyond basic nutrition" (Hasler 2002; Abdel-Salam 2010). In 1999, the American Dietetic Association (ADA) defined functional foods as complete, fortified, enriched foods or perfected foods which provide health benefits in addition to providing essential nutrients (e.g., vitamins and minerals), when consumed in effective levels on a regular basis, as part of a diversified diet

(Hasler 2002; ADA 2009; Abdel-Salam 2010).

Later, organizations such as the Food and Drug Administration (FDA) and the European Food Safety Authority (EFSA) felt the need to clarify the concept of health benefits, explaining that functional foods are not intended to treat, cure, diagnose or mitigate diseases because those features are attributed to drugs (Schneeman 2007; Bento 2008). This need for clarification is needed because the importance of the diet in many chronic diseases is variable (Hasler 2002; Holm 2003). In fact, chronic diseases are the result of many factors, such as the diet, behavior, environment, and genetic characteristics of each individual (Bento 2008).

The discovery that many foods contained bioactive components that were not always physiologically effective when integrated into a complete diet, or that were only suitable for certain age groups, has led to only foods whose physiological effects have been scientifically proven being granted the status of functional food (Milner 1999; Hasler 2002; Weststrate and others 2002; Bento, 2008). This proof follows the criteria that were first proposed in the United States by the FDA in 1999 (Thomas and Earl 1994; Hasler 2002; Bento 2008), which later were also suggested for the European Union with some adaptations. The claim of health benefits, in Europe, can only be authorized by the EFSA after undergoing a rigorous scientific evaluation (Bento 2008).

The agricultural food sector has recently discovered that functional foods are a business opportunity, since these products have high added value, and can be sold at prices far above those of similar products that do not have functional characteristics (FAO 2002, Pinto 2010).

There are five main markets for functional foods, namely beverages, dairy products, confectionery products, bakery products, and breakfast cereals.

Market evolution and current status

Functional foods have recently become widely available. The market is growing, new products are continuously being launched, and competition is becoming more intense. Consumers have more choices available, and thus the potential for differentiation and attractiveness of the product becomes extremely important (Schmidt 2000).

The design and development of functional foods is a process consisting of gradual steps: research, development, and marketing (Roberfroid 2000b).

The market for functional foods began to develop in Japan in a more contextualized way, representing this type of food as a class apart properly labeled as FOSHU, and different from traditional foods. The Western concept of functional foods, however, does not separate them from traditional foods, acknowledging only that this kind of food provides added functionalities. The increased interest in functional foods is a result of the increase in the cost of health maintenance, given the increasing life expectancy, and also the interest of older people in extending their quality of life (Menrad 2003; Siró and others 2008). The recognition that such products can enhance the quality of life and reduce some disease risks , began to stimulate the market which, however, shows greater growth in the United States than in European countries. The European market is heterogeneous, however, being higher in northern countries than in Mediterranean countries, where consumers show a greater preference for natural and fresh products (Menrad 2003; Siró and others 2008).

The major areas of development for functional foods are related to the following:

gastrointestinal health and immunity; prevention of cardiovascular diseases; cancer prevention; weight regulation, insulin sensitivity and control of diabetes; bone health and prevention of osteoporosis; mental and physical performance. Currently, the functional food market is dominated by products that influence intestinal health and, within these, probiotics represent a large share of this market, especially lactic acid bacteria and bifidobacteria (Siró and others 2008). They are often added to dairy products, being the functional dairies segment one that presents some of the biggest innovation in products (Menrad 2003). Prebiotics, such as previously described, constitute another important group of functional products. They have the ability to stimulate the growth of microorganisms in the colon, increase the feeling of fullness, participate in the prevention of obesity, and also contribute to the regulation of blood glucose levels. Beverages fortified with vitamins A, C, and E and with calcium, or products enriched with phytosterols or fat acids such as omega-3 or conjugated linoleic acid (CLA), constitute a different range of products that tend to be used for the prevention of cardiovascular diseases, obesity, and osteoporosis and currently present a major growth in functional food consumption (Menrad 2003; Siró and others 2008). Although the marketing of these foods as being functional represents an important asset for these products, their development is complex and expensive because it requires significant research efforts. It involves such steps as: the identification of products with functional activity; assessment of their physiological effects; incorporation into a suitable food matrix; the maintenance of their bioefficiency and sensory quality after technological processing of the product or meal preparation; and the conduction of clinical trials and consumer education (Weststrate and others 2002; Siró and others 2008).

Several multinational companies, often in collaboration with manufacturers of specialized ingredients, are already established in the market. However, smaller companies are already able to create and defend a place in the market. Soft drinks and dairy products are the categories that lead the market from the standpoint of sales, while energy drinks are the main products that benefit health (Price Water House Coopers LLP 2009).

Nowadays, the main markets for functional foods are Japan, the United States, and Europe. It is estimated that in 2005 the worldwide market for functional foods handled about €45 billion in Europe, Japan, and the United States, the latter representing €11 billion. In the United States in 1980, soybean extract (or soy milk) gave a turnover of €1.5 million. In 2001, it reached a value of approximately €380 million. In 2006, products fortified with soy amounted to a total of €2 billion. The participation of the functional foods in the market is also growing. In the United States in 1998, growth was estimated as 10.7% over the previous year. On the world market in 1999, the annual growth rate was estimated at 1% (Menrad 2003).

Recent estimates show that growth for this sector in the United States is in between 8.5 and 20% per year above the global market, where growth is estimated at between 1 and 4% per year (Price Water House Coopers LLP 2009).

A comparison between the revenues of functional foods in the United States in 2002 and in 2007 by food category is shown in Table 25.1. It can be verified that for bakery products and cereals, there was an increase in sales of 8% between 2002 and 2007.

Table 25.1 Revenue of functional foods in the United States by food category, 2002–2007 (Adapted from Price Water House Coopers LLP 2009)

	Revenue (billions of euros)		Compound annual growth rate (%)
	2002	**2007**	**2002–2007**
Soft drinks	4.1	7.2	12.3
Dairy products	3.5	5.1	8.1
Bakery and cereals	2.3	3.5	8.0
Confectionery	1.3	1.7	6.7
Savory snack	0.7	0.4	1.5
Others	2.1	2.6	3.6
Total	14.0	20.5	8.5

Foods that help increase energy levels represent 29% of the market for functional products that benefit health. These products tend to have attributes that consumers can feel quickly, which contributes significantly to their popularity.

Products that benefit intestinal, bone, and heart health have a considerable market share and are usually bought by older consumers. Other functional foods include products that aid weight control, help with mental faculties, and improve child health. These products tend to be sought by younger consumers, particularly by parents or expectant parents (Price Water House Coopers LLP, 2009).

A comparison between the revenues in 2002 and 2007 in the United States from functional foods that benefit health is shown in Table 25.2.

Table 25.2 Revenue of functional foods in the EUA by benefit to health, 2002–2007 (Adapted from Price Water House Coopers LLP 2009)

	Revenue (billions of euros)	Compound annual growth rate (%)	
	2002	**2007**	**2002–2007**
Energy	4.4	6.0	6.2
Heart health	2.7	3.8	6.9
Bone health	2.1	2.8	5.3
Intestine health	0.3	0.5	15.8
Others	4.1	7.5	12.5
Total	13.6	20.6	8.5

The main categories of foods, soft drinks, and dairy products in the US market are shown in Figure 25.1. The soft drinks category includes energy drinks, water enriched with vitamins, and other beverages. The functional dairy product market is expected to grow about 5–15% annually over the next 4 years, surpassing the market for non-functional dairy products.
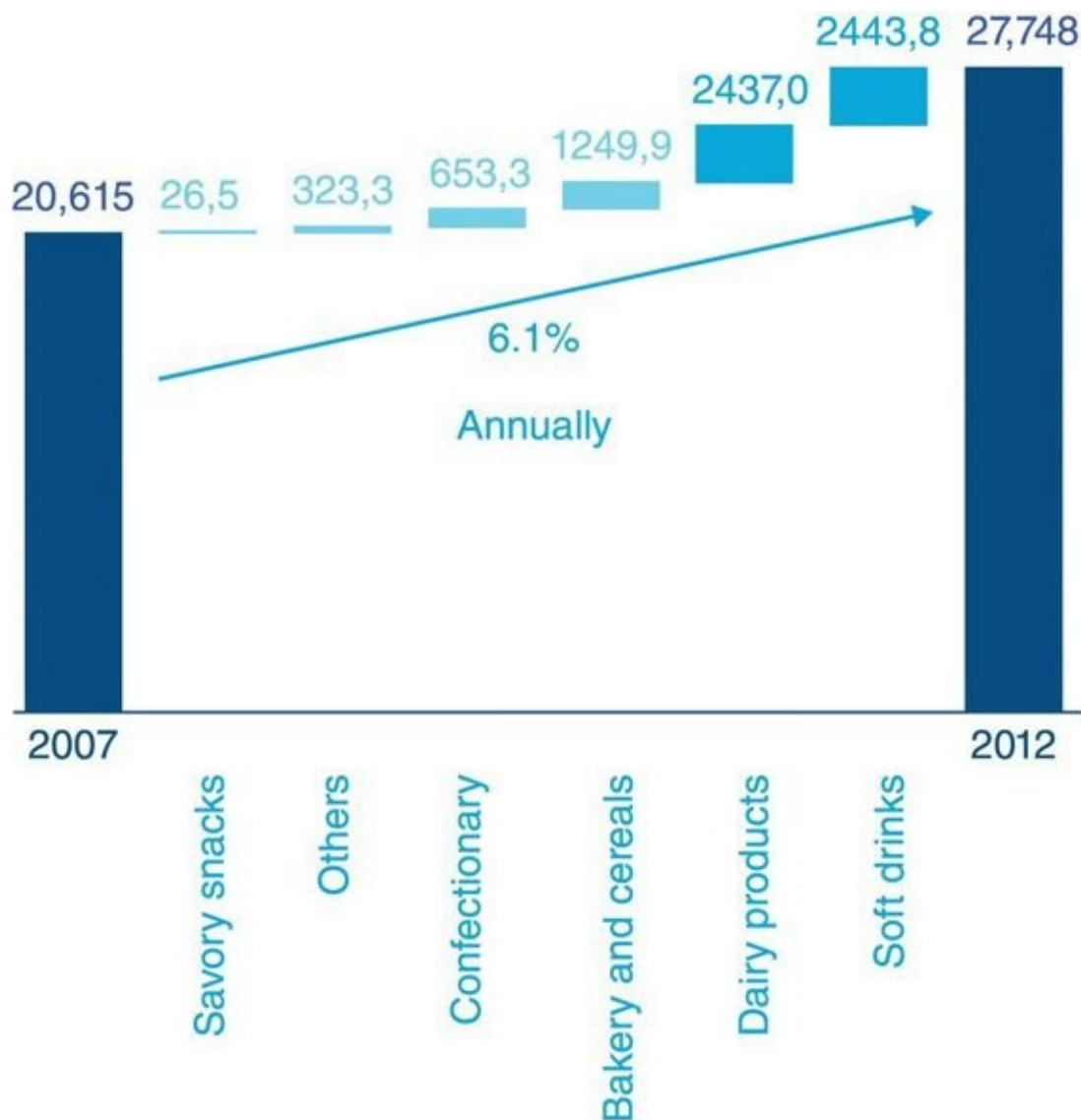
Figure 25.1 Graphical representation of the growth for the functional products in the US market between 2007 and 2012 (in million euros). Soft drinks and dairy products are the products which lead the market, followed by bakery products and cereals (adapted from Price Water House Coopers LLP 2009).

According to available estimates, the market for functional products in Europe surpasses the volume of €1.5 billion. Should a broader definition be used, it is estimated that the European market for functional foods is about €3–6 billion. This means that in Europe, the current market share for functional foods is less than 1% of the total market for food and beverages.

In Europe, the most important countries within the functional food market are Germany, France, the United Kingdom, and the Netherlands (Menrad, 2003).

In Portugal, consumers have been discovering these types of foods. In 2007, a total of 3.4 million households purchased functional foodstuffs, which represents a penetration rate of 90%, according to a study by TNS. Despite being more expensive than so-called "normal" food, the functional food category has above average growth, and, during this period, the Portuguese spent €200 million on the purchase of these products, 12.8% more than in the previous year. Figure 25.2 depicts the consumption of functional products in Portugal in 2007. It can be verified that fruits and vegetables, although not industrially manufactured products, are those with the highest percentage of consumption, followed by dairy products (milk and yogurt). The bakery products and pastries, such as bread, crackers, and wholegrain

cereals have only a percentage of 1.2%, 3.7%, and 3.7%, respectively.
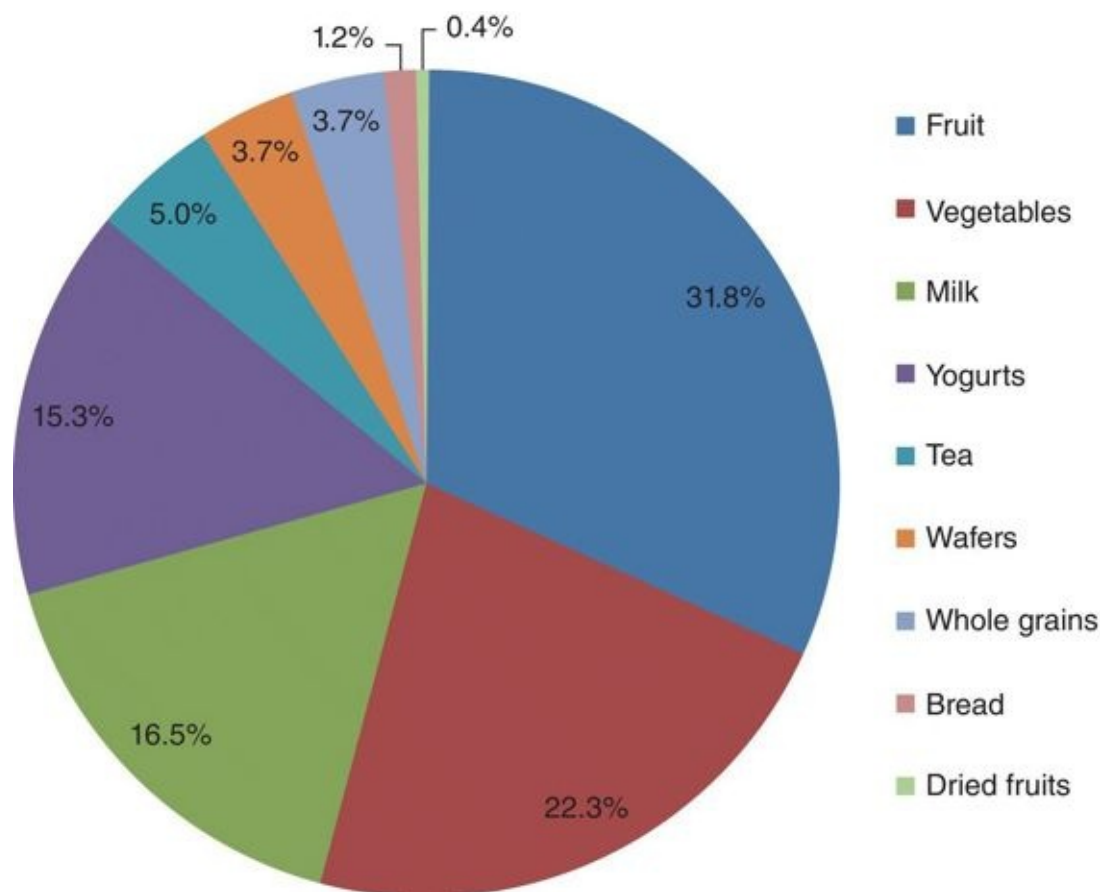
Figure 25.2 Graphic representation of functional food consumption in 2007 in Portugal (percentage) (Adapted from Oliveira 2008).

The frequency of purchase of functional items per household increased by 1.6% in 2007, as well as the average spending per transaction, which increased 4.77% from €4.54 to €4.77.

Baking process

The bread making process has three phases: crushing, fermentation, and baking. Of all the cereals – wheat, rye, barley, oats, corn, and rice – only wheat and rye are important for obtaining well-structured bread (Pinto 2010). The essential ingredients needed to obtain the bread, however, are wheat flour, water, salt, and yeast.

Wheat flour is the structural component of the dough and is the key ingredient for obtaining bread. Wheat flour has proteins – gliadin and glutenin – that have unique functional properties and are capable of forming gluten. Gluten is formed when flour, water, and the other bread ingredients are mixed and undergo the action of mechanical work. As the water begins to interact with the wheat's insoluble proteins (gliadin and glutenin), gluten begins to form. The advantage of gluten in baking processes is strictly tied to its ability to give consistency and elasticity to the dough, as well as retaining the CO_2 formed during fermentation, which results in the desired increase in volume.

The gliadins are single-chain proteins, extremely sticky, and are primarily responsible for the consistency and viscosity of the dough and also control the volume of bread. Glutenins have branched chains and are responsible for the extensibility of the dough. The amount of these two proteins in wheat is crucial to the quality of the gluten formed in the baking process.

Thus, it is sometimes necessary to enrich low-protein flour with gluten to ensure the quality of the bread.

Water is of paramount importance in dough formation. After hydrating the flour, water ensures the union of the proteins that generate gluten which, at the same time, provides a suitable environment for the development of enzymatic activity and consequently, bread fermentation. This enables the formation of the gluten, controls the temperature and consistency of the dough, heating it or cooling it, dissolves salts, suspends and distributes the ingredients, moisturizes and increases the volume of starch and enables the action of enzymes.

Salt controls fermentation and strengthens the flour gluten, since gliadin, one of its components, has a higher solubility in salt water, which provides a greater formation of gluten. It is also bactericidal, is decisive in the hydration of the dough, acts as flavor enhancer, and brightens the bread crumbs.

The yeast commonly used in bakeries is fresh, and comes from *Saccharomyces cerevisiae* species. In the baking process, its main function is to ferment sugars, producing CO_2, which at the same time is responsible for the formation of internal alveoli and an increase in the dough's volume. Industrially, yeast is produced from molasses using yeast cultures suitable for its reproduction.

The baking process begins with mixing. In this stage, the ingredients are homogenized, aeration takes place and the dough undergoes mechanical work, thus starting the development of the gluten formed by the hydration of flour proteins until a dough with adequate viscoelastic properties is obtained. A suitable temperature at the end of the mixing is 26−28 ºC, since this inhibits fermentation and subsequent excessive gas production, being the dough´s temperature during mixing controlled by the temperature of added water.

Afterwards, the main fermentation takes place which is an alcoholic and anaerobic fermentation produced by the action of the yeast on the sugars present in dough. During the main fermentation, carbon dioxide is produced and physicochemical modifications take place that interfere with the plastic properties of the dough, leading to the formation of the taste and flavor of bread, as well as contributing to its conservation. Fermentation lasts for about 2−3 h depending on the temperature and the dough composition. To ensure predominance of this type of fermentation, the dough should exit the mixer at a temperature between 25 and 28 °C and be maintained at 27 °C in a fermentation chamber at 75% relative humidity (Pinto 2010).

After fermentation ends, the physical procedure of division takes place, which may be performed manually or mechanically. This produces portions of dough with appropriate weight, suited to ensure uniformity of the final product, and the scaling that ensures the formation of a solid surface, thus eliminating the viscosity of the dough, and also giving it a regular shape, thus easing handling during subsequent stages of processing.

After this stage, we enter the secondary fermentation. The objective of this step is to recover part of the extensibility lost during division and molding. The portions of dough that have been shaped are sent to the fermentation chamber where they rest for 5−20 min at an optimum temperature of 26−30 °C and a relative humidity of 75−80%. If the temperature in the fermentation chamber is below the optimum temperature, the fermentation process slows down. If, however, the temperature is above the optimum temperature the gas holding

capacity is reduced. A low relative humidity causes the dough to dry out, unlike a high relative humidity which makes the dough sticky and difficult to handle.

Then we proceed to the molding which improves the texture and structure of the bread as well as allowing the product to acquire an appropriate shape. Typically, modulators are used, designed to degas, flatten, roll and seal the dough, the most common being the one with rollers. However, this operation can also be performed manually.

After molding, the final fermentation takes place in chambers with suitable temperature and humidity conditions, and usually lasts about 40–120 min, depending on the type of bread, formulation, and quality of the flour. Since the dough loses gas during molding, it is essential to allow the dough a final rest so that it regains an adequate volume. This has a direct influence on the quality and texture of the cells of the core of the final product.

When the temperature inside the bread reaches 60 °C, the yeast is inactivated and fermentation is complete, thus cooking starts. Cooking is the thermal treatment of the starch and protein, leading to inactivation of the enzymes, allowing the formation of crust and the development of flavor and taste. This process occurs at temperatures between 200 and 230 °C for a variable time, depending on the size and type of the bread being baked.

When the cooking process is complete, the bread is placed in the cooling chamber until it reaches room temperature, before being subjected to slicing (for a loaf of bread) for subsequent packaging. Cutting hot bread may cause deformation, while packaging bread while it is still warm results in condensation, the subsequent growth of fungi, and other deterioration. Therefore, the dough is allowed to cool for about 1 h and is then ready to be cut, wrapped, or bagged.

Functional ingredients for baking industry

Nowadays, consumers are increasingly interested in their personal health, and expect their food to be healthy and to prevent illness. At the same time, new products with new organoleptic properties must be developed to address market needs. The use of functional ingredients may fulfill these demands. A great variety of functional ingredients can be introduced in food products, depending on the aim of that incorporation. Fibers, flavors, vitamins, minerals, bioactive compounds, prebiotics, and probiotics are some of the most used compounds used to add value to food products (Ubbink and Krüger, 2006; Dewettinck and others 2008; Kadam and Prabhasankar 2010).

The bakery industry encompasses a wide variety of products as breads, rolls, buns, crumpets, muffins, bagels, pancakes, doughnuts, waffles, and cookies and other filled products such as fruit and meat pies, sausage rolls, pastries, sandwiches, cream cakes, pizza, and quiche. These products are mainly composed of raw materials such as wheat flour, water, yeast, salt, and other ingredients. The constant growth in the bakery industry has been driven by consumer demand. Consumers ask for convenient, premium baked goods that, as well as being fresh and conveniently packaged, should also be shelf-stable. Recently, nutritious and functional bakery products have been developed with an increasing amount of functional products. This kind of product allows the fortification of bakery products that confers health benefits for the consumers, but also improves their properties to achieve a longer shelf-life and improved organoleptic properties (Smith and others 2002).

However, the modification of the recipe by the incorporation of functional ingredients and the alteration breadmaking process (e.g., conventional or direct, frozen dough, frozen partially baked bread) has a significant impact in the properties of the final product, such as the alteration of its nutritional value (e.g., glycaemic index, protein quality, and bioavailability of some minerals) (Sivam and others 2013). The application of new functional ingredients requires a deep study of their influence on the properties of food products (e.g., freshness, appearance, and sensory properties) as well as on their active properties, such as biological functionality.

Some of the functional ingredients investigated in the most recent studies and used in the bakery industry are mentioned here.

Polysaccharides and fibers

Polysaccharides and dietary fibers have been among the most studied ingredients in bakery products due their nutritional capacity and their ability to improve texture, organoleptic properties, and act as stabilizers, which are some of the properties that lead to a better quality product. The main studies are related to the replacement of traditional ingredients with dietary fibers and non-starch polysaccharides. Dietary fiber is an ingredient from the new generation of functional food products, which meet consumer demands. The incorporation of these ingredients in bakery products has lead to a great number of food applications. The role of food structure in the development of structured products with low starch digestibility, and the replacement of starch with other non-digestible polysaccharides are among the main areas of research by the scientific community and the food industry (Autio and others 2004).

It is important to refer to the ambiguous definition of dietary fibers, which is one of the challenges of the scientific and regulatory communities. Initially, dietary fiber was considered only as a substance obtained from cell wall material; however, this consideration has now expanded to include all indigestible polysaccharides (e.g., gums, modified celluloses, oligosaccharides, and pectins), by considering not the origins of the materials but by highlighting their physiological behavior (that is, edible and not digested and absorbed in the small intestine) (Brummer and Cui 2005).

The use of composite flour for bread making is gradually gaining prominence worldwide for various economic and nutritional reasons. Recently, several studies have been made of the influence of mixtures of polysaccharides and fibers on the physicochemical properties of bakery products and their relationship with sensorial properties and nutritional advantages.

Recently, resistant starch (RS) has been discovered as a new source of dietary fiber. Different RSs have been identified: RS1 (a physically inaccessible starch found in starchy foods), RS2 (native resistant starch granules), RS3 (retrograded starches) and RS4 (chemically modified starches). For industry applications, however, only RS2 (e.g., Hi-maize 260) and RS3 (e.g., Novelose 330) are available as commercial ingredients in the market (Sanz and others 2008; Fuentes-Zaragoza and others 2010). Recently, studies have evaluated the use of RS on the properties of some bakery ingredients and products to verify the effect of this new ingredient (Sanz and others 2008; Korus and others 2009; Hong and Yoo 2012).

Wheat flour (WF) was tested with different concentrations of RS and their rheological properties were evaluated. The results obtained suggested that the presence of RS (at various concentrations) modifies the rheological properties of WF, the most evident changes being observed for WF mixed with the highest RS concentration (20%) (Hong and Yoo 2012). Sanz and others (2008) studied the replacement of wheat flour by different types of RS on muffin batter rheology and on baked muffin height, volume, and number of air bubbles. The utilization of different RS affected the properties in a different ways, which were related to their different baking performances. Although acceptable, the baking performances of the muffins with RS were lower than the control muffins (Sanz and others 2008). The partial replacement of corn starch by tapioca and corn RS preparations was studied in gluten-free breads. The utilization of RS showed a more elastic character of the dough, and the modified doughs displayed higher starch gelatinization temperatures and lower viscosities proportional to the RS portion. Also, the crumb was less hard when RS was incorporated. The most relevant changes were found for the values of total fiber and insoluble dietary fiber in bread with RS, which increase up to 89% and 137%, respectively, when compared with bread without RS replacement (Korus and others 2009).

Some non-starch polysaccharides and fibers have also been tested as functional ingredients for bakery products. Gums (e.g., xanthan, guar gum, and locust bean gum) used in the food industry as thickeners and stabilizers, have received a great attention from nutritionists due the possibility of using them as a dietary supplements. Guarda and others (2004) have tested four different hydrocolloids (sodium alginate, xanthan, k-carrageenan, and hydroxypropylmethycellulose (HPMC)) during the bread making process, and studied their effect on fresh bread quality and their influence on bread staling. Results showed that different hydrocolloids lead to different effects on bread quality. HPMC improved all the parameters tested: specific volume index, width/height ratio, and crumb hardness; in addition, good sensory properties were obtained for visual appearance, aroma, flavor,

crunchiness, and overall acceptability. All hydrocolloids were also able to reduce the loss of moisture content during bread storage, reducing the dehydration rate of crumb. In addition, alginate and HPMC showed an antistaling effect during storage, retarding crumb hardening (Guarda and others 2004). In a similar study, Shittu and others (2009) studied xanthan gum as a bakery ingredient, and its influence on the properties of dough and bread from composite cassava–wheat flour. The results showed that the presence of xanthan gum affects the dough tenacity and extensibility and sensory acceptability of fresh composite bread. The addition of xanthan gum lead to bread samples with more open crumb structure and better sensory acceptability (Shittu and others 2009). The effect of inulin addition on the rheological properties of common wheat dough and bread quality was also evaluated. Results showed that the flour replacement by inulin at different levels change dough machinability, viscoelasticity, and bread making performances. Bread making process depends on the inulin type and on the concentration added. So the addition of inulin could be an effective way to produce functional white flour bread without negatively changing its desirable physical properties (Peressini and Sensidoni 2009).

Angioloni and Collar (2011) have studied the influence of the physicochemical properties of mixtures of hydrocolloids (cellulose derivates and galactomannans) and prebiotics in hydrated wheat flour matrixes, and discussed their nutritional and technological functional profiles. The technological, functional, and some nutritional bread properties were found to depend on the molecular characteristics of dietary fiber. Dietary fibers with a larger particle size and high viscoelastic profile in highly sensory acceptable breads with a higher amount of resistant starch, result in a lower digestible starch, a lower than expected in vitro glycaemic index, and slightly lower protein digestibility (Angioloni and Collar 2011).

Mandala and others (2009) have tested many ingredients to develop products that have both high nutritional value and good storage stability during freezing. The main propose was to verify if the presence of other functional ingredients presented similar physical characteristics to the commercial product. Breads with hydrocolloids (HPMC or locust bean gum), commercial soluble fibers (inulin and polydetrose) or whole oat flour were prepared, and also contained commercial shortening with plant stanols (benecol–olive oil and plant stanol). The physical characteristics of frozen dough and semi-baked frozen samples were determined after baking and comparisons to fresh samples were performed. Fresh samples containing hydrocolloids, polydextrose or commercial shortening presented similarities. Semi-baked breads had an elastic crumb (e.g., inulin-containing breads had an 18% increase in crumb elasticity compared to the respective fresh ones). Control and inulin semi-baked breads showed more pronounced differences (e.g., 60–80% lower crust firmness values than those of fresh samples). Samples containing whole oats presented an increased water adsorption capacity at high a_w, as observed by sorption isotherms and a water-binding capacity change after storage (Mandala and others 2009).

In 2009, Hu and others studied the use of two types of fibers as functional ingredients in bakery products. Defatted rice bran was used to prepare hemicellulose B and an insoluble dietary fiber that were then added to bread formulations at different concentrations and compared with a control. Defatted rice bran hemicellulose B showed a high water-binding and swelling capacity as well as a high fat-binding capacity; however, it had a low viscosity. The addition of increasing concentrations of this fiber reduced the loaf volume and increased the firmness of the breads. Sensory evaluations revealed that breads containing both types of

fibers at different concentrations were acceptable overall, confirming their potential in the development of functional bakery products (Hu and others 2009).

Mango dietary fiber concentrate showed good properties for use as fiber in human diets and was tested in bakery products. Results showed that bakery products prepared with the mango fiber conserved the balance of soluble and insoluble dietary fiber. In vitro starch digestibility tests of the bakery products indicated a low predicted glycemic index showing that mango fiber can be an alternative for the development of products with balanced dietary fiber components and low glycemic response (Vergara-Valencia and others 2007).

Currently, new materials such as polysaccharides and fibers are among the most studied functional ingredients for bakery products, appearing in the market as good options for the development of functional foods; however, other products (e.g. prebiotics, oils, antioxidants, minerals, and vitamins) are available and also seem to have great potential.

Prebiotics and probiotics

Prebiotics and probiotics are used in food industry, sometimes without any distinction, and although both benefit digestive health, they are very different. Probiotics have been defined as "Live microorganisms (bacteria or yeasts), which when ingested or locally applied in sufficient numbers confer one or more specified demonstrated health benefits for the host" (FAO/WHO, 2002). Prebiotics, on the other hand, act as the "food" for these beneficial probiotic bacteria, enhancing their activity. Prebiotics are compounds, usually oligosaccharides, which cannot be digested by enzymes of the upper gastrointestinal tract but are fermented selectively by some types of intestinal bacteria in the large intestine, typically bifidobacteria and/or lactobacilli. This activity results in beneficial health effects, including reduced gut infection, better absorption of minerals, and suppression of colon cancer initiation (Charalampopoulos and Rastall 2012).

Probiotic cultures can be used to stimulate the growth of certain microorganisms, reducing potentially harmful bacteria that can lead to the reinforcement of the natural defense mechanisms of the human gut. Due to their claimed health benefits, probiotics have been incorporated into a range of food products (e.g., dairy, cereals, and chocolate) for delivery to the human gut. The use of probiotics is not new to dairy industry; however, their use in bakery products is very recent, and a challenge for the industry. Moreover, several problems exist concerning their viability in foods because of their sensitivity to heat, moisture, and oxygen, needing their protection during the baking process (Anal and Singh 2007; Burgain and others 2011). Their main problems in bakery products are their viability and sensitivity to the high temperatures during that occur baking. Recently a new methodology combining microencapsulation and edible coatings has been successfully tested for protecting *Lactobacillus acidophilus* during baked bread production. *Lactobacillus acidophilus* was microencapsulated using a mixture of whey protein isolate : CMC : pectin using a spray-drier. After encapsulation of the microorganism, a starch coating was used and applied to the bread surface. The results showed that in all tests, *L. acidophilus* survived the baking process and storage. Sensory evaluation of the breads showed that the functional breads have good acceptability; however, the presence of the coating changed the properties of the bread crust (that is, increases the water activity and reduces the failure force of the bread crust) (Altamirano-Fortoul and others 2012).

Immobilization is another methodology used, but with inconclusive results. Plessas and others (2007) used brewer's spent grains for the immobilization of baker's yeast, kefir, or *Lactobacillus casei* to produce new types of bread (produced by the straight-dough and by the sourdough method) with functional properties. Results showed that the breads produced had good quality and remained fresher for longer, compared to commercial-type baker's yeast bread, with the best results (higher moisture retention during baking, lower rates of water evaporation and staling, and maintenance of freshness for longer) obtained for sourdough breads. Also, consumer evaluation showed a high preference for the sourdough breads when aroma, taste, and overall quality were evaluated. The extension of shelf-life (reduction of staling rate and increase of microbial stability) and the potential probiotic properties of bread made with immobilized kefir and *L. casei*, were, however, not investigated and were a drawback of this work (Plessas and others 2007).

Meanwhile, new fermentation cultures with probiotics have been tested because of their capacity to improve the quality and level of lysine, the availability of the vitamin B groups, as well as the degradation of phytates (Soccol and others 2010). Phytic acid (one of the major storage forms of phosphorus in cereals, legumes, and oil seeds) is typically found in bakery ingredients and inhibits mineral (iron, zinc, calcium) absorption (Bohn and others 2004).

In 2009, Sanz-Penella and others studied the utilization of a combination of *Bifidobacterium pseudocatenulatum* and *Bifidobacterium infantis* with high phytatedegrading activity as starter cultures in breads. Using standard conditions and a direct-method breadmaking process, the nutritional, technological, and sensorial quality of the final products was compared with control samples (samples in the absence of bifidobacteria and samples supplemented with commercial fungal phytase). Results showed that the bread fermented with the bifidobacterium strains had similar technological and sensorial qualities as the controls and had lower levels of phytates. The use of strains *Bifidobacterium* proved to be a good strategy for reducing the content of phytates in bakery products with high levels of bran (Sanz-Penella and others 2009).

Different approaches have been adopted to fortify bakery products with prebiotics. The most frequent is the incorporation of prebiotics in the initial formulation. Angioloni and Collar (2011) have studied the influence of the physicochemical properties of mixtures of hydrocolloids (cellulose derivates and galactomannans) and prebiotic oligosaccharides (fructo- and glucooligosaccharides) in hydrated wheat flour matrixes. The technological, functional (sensory firmness and overall acceptability) and some nutritional bread properties (protein digestibility, rapidly digestible starch, slowly digestible starch, in vitro expected glycemic index, total digestible starch, and resistant starch) were found to depend on the molecular characteristics of the dietary fiber (mean particle diameter, storage modulus, loss modulus, complex viscosity, and lactic acid solvent retention capacity) (Angioloni and Collar 2011).

Izydorczyk and others (2008) studied the performance of barley fiber-rich fractions (as high dietary fiber ingredients) in two-layer flat bread. They evaluated the effects of particle size reduction by pin milling on the functional properties of the fiber and showed that pin milling the fibers significantly reduced their particle size, increasing the solubility of β-glucans and arabinoxylans (added to enrich the fiber in non-starch polysaccharides). Results showed that the addition of 20% of barley fiber to wheat flour significantly increased dough water absorption and weakened the dough properties. However, the barley fiber-enriched doughs

exhibited good handling characteristics at the dividing and sheeting stages. The appearance, diameter, layer separation, crumb, and aroma of the barley fiber-enriched flat breads were comparable to that of the control (Izydorczyk and others 2008).

Recently, a very interesting work studied the in situ production of cereal-derived arabinoxylan oligosaccharides (AXOS) during bread making. Initially, the capacity of different xylanases to produce AXOS was compared in whole meal bread making. Three mesophilic xylanases originating from different microorganisms were used at different dosages. The thermophilic xylanase from *Hypocrea jecorina* solubilized and cleaved the arabinoxylan fraction to the largest extent, resulting in an AXOS content of 2.1% (dry basis) and an average degree of polymerization of 9. Then, the impact of thermophilic xylanase from *H. jecorina* on the AXOS levels in dietary fiber enriched breads was studied. In conclusion, rye or wheat bran fortified breads treated with thermophilic xylanase from *H. jecorina* yielded good quality breads with AXOS levels above 2.0% with an average degree of polymerization of 26 and 19, respectively (Damen and others 2012).

While prebiotics seem to be a ingredient that can be added to a bakery product without problems, more studies need to be made not only to evaluate the effect of probiotics cultures on the properties of bakery products, but also to study the viability of those cultures after baking.

Oils and lipids

Fats and oils are important ingredients in bakery products being their major functions: tenderize the product and soften the texture, add moisture and richness, add flavour and to assist in leaving when used as creaming agents (Lu and others 2010). From the nutritional point of view, lipids function as sources of metabolic energy and as carriers of fat-soluble vitamins (A, D, E, and K).

Bakery fats (i.e., shortening, margarine, or cooking fats) are tailored fat systems whose nutritional and functional properties have been manipulated to deliver specific consumer needs. The functional characteristics of natural fat systems have been modified to provide the desired consistency and keeping quality to baking, confectionery, and cooking applications. These fats are mostly prepared from vegetable oils by hydrogenation (Lee and others 2008). Note that vegetable oils and solid fats are different constituents. Solid fats come from both animal and plants sources and are usually solid at room temperature. Oils are produced mainly from plants and are liquid at room temperature. The most usual oils used in the bakery industry are extracted from seeds (e.g., safflower, sunflower, sesame, canola, and flaxseed), beans (e.g., peanut, soy), grains (e.g., corn, wheat germ), fruits (e.g., avocado, olive) and nuts (e.g., almond, coconut, walnut, and palm kernel) (Ghotra and others 2002). An example of the oils incorporated in bakery products is omega-3 oils. These oils have potential applications in health promotion, such as: prevention of atherosclerosis, protection against arrhythmias, reduction of blood pressure, beneficial for diabetic patients, fight against manic-depressive illness, reduction of symptoms in asthma patients, protection against chronic obstructive pulmonary diseases, alleviation of symptoms of cystic fibrosis, prevention of various cancers, provision of bone health, and improvement to brain functions in children (Kadam and Prabhasankar 2010).

Vicario and others (2002) analyzed the fatty acid compositions of 39 brands of cookies and

bakery products with special attention to the their trans-fatty acid content. The average contents (percent wet weight of the total fatty acids detected) for the different nutritional fractions were as follows: saturated fatty acids (SFA), 49.43%; monounsaturated fatty acids (MUFA), 32.87%; polyunsaturated fatty acids (PUFA), 12.48%; and trans-fatty acids (TFA), 5.20%, the mean fat content being 22.7. These authors observed that the fat used to elaborate the samples was mainly composed of vegetable and animal fat, and only in a few samples were partially hydrogenated vegetable oils used as the main source of fat (Vicario and others 2002). In a similar work, Parcerisa and others (1999) analyzed the fatty acid composition of 15 samples of the most common industrial bakery products sold in Spain. SFA occurred in the largest proportions in all samples (52.8%), followed by MUFA (23.5%) and PUFA (17.2%). A small percentage of TFA were found in all samples, with a mean value of 5.7% (Parcerisa and others 1999).

Papantoniou and others (2003) used fractionation and reconstitution techniques to study the contribution of endogenous flour lipids to the quality of semisweet (Rich Tea-type) biscuits. Biscuit flour was defatted with chloroform and baked with bakery fat but without endogenous lipid addition. The authors concluded that the polar and non-polar lipid fractions had positive effects in restoring flour quality, but the polar lipid fraction was of the greatest benefit (Papantoniou and others 2003).

There are various methods for placing fats and oils into classes. As a result, the classification of fats and oils varies according to their end use. Different parameters may be used to classify shortenings and margarines, fats may be classified by fatty acid chain lengths, degree of unsaturation, source, and consumption.

Simple lipids include free fatty acids (FFA) as well as monoacylglycerols (MAG) , diacylglycerols (DAG) and triacylglycerols (TAG). While, saturated FA (e.g., palmitic and stearic acids) have no double bonds between adjacent fatty acid carbon atoms, unsaturated FA have one (monounsaturated) or more (polyunsaturated) double bonds. The most common FA species in many acylglycerols are palmitic, stearic, oleic, and linoleic acids (Pareyt and others 2011).

Antioxidants

Antioxidants have become an essential group of food additives mainly because of their unique property of enhancing the shelf-life of food products without any damage to their sensory or nutritional qualities. One of the principal factors limiting the shelf-life of food products is lipid autoxidation, which leads to the development of rancidity and off-flavor (Nanditha and Prabhasankar 2009). This lipid autoxidation can be delayed or eliminated by using antioxidants. The selection of antioxidants that can be used in food are determined by important factors such as legislation, cost, stability, effectiveness, and the consumer preference for natural antioxidants (e.g., vitamin C and tocopherols) (Rafecas and others 1998). However, the use of synthetic antioxidants, for example propyl (PG), octyl (OG) and dodecyl (DG), tert-butylhydroquinone (TBHQ), butylated hydroxytoluene (BHT), and tert-butylhydroxyanisole (BHA), is widely used due their low cost and high stability in contact with the fats and oils used as ingredients for bakery products (André and others 2010).

Antioxidants can be classified as primary and secondary or as processing antioxidants. Primary antioxidants terminate the free-radical chain reaction by donating hydrogen or

electrons to free radicals and converting them to more stable products (Nanditha and Prabhasankar 2009; André and others 2010). The primary antioxidants include hindered phenols, phenols, and other miscellaneous antioxidants. Secondary antioxidants allow the decomposition of lipid peroxides into stable end products. These antioxidants include organophosphites and thioester (André and others 2010).

Different requirements must be followed to use antioxidants in baked foods: they should have a very low toxicity, not affect the flavor or appearance of the end product, be effective at low concentrations under normal conditions of processing and storage, must be stable at high temperature for certain applications such as frying and baking, and should be soluble and dispersible in end products (in emulsions and other preparations) that contain water (André and others 2010). Some antioxidants usually used in the bakery industry and their principal characteristics are presented in Table 25.3 and discussed later.

Table 25.3 Antioxidants applied in bakery industry

		Examples	References
Primary antioxidants	Phenols	Gallates	Guldborg 1981
		Tertiary butyl hydroquinone	André and others 2010
	Hindered phenols	Butylated hydroxy anisole	Ou and others 2010
		Tocopherols	Quílez and others 2006
		Gum guaiac	Grettie 1933
	Miscellaneous primary antioxidants	Ethoxyquin	Kwak and Kang 2006
		Trolox-C	Zielińskiand others 2012
Secondary antioxidants	Oxygen scavengers	Ascorbic acid	Andréand others 2010
		Ascorbyl palmitate	Pizarro and others 2006
	Chelating agents	Polyphosphates	Watts 1950
		Tartaric acid	Kohajdová and Karovičová 2009
		Citric acid	André and others 2010
	Secondary antioxidants	Thiodipropionic acid	André and others 2010
		Dilauryl thiodipropionate	Sivam and others 2010
	Miscellaneous antioxidants	Nitrites	Nabrzyski and others 1990
		Spice extracts	Reddy and others 2005
		Flavonoids	Balasundram and others 2006
		β-carotene	Quílez and others 2006
		Zinc	Frontela and others 2011

Tocopherols

Tocopherols, collectively known as vitamin E, are lipid-soluble natural antioxidants that are widely distributed in plant tissues such as nuts, fruits, and vegetables. The tocols and tocotrienols include α, β, γ and δ homologs. These homologs have a basic structural unit of a 6-chromanol ring with a phytol side chain and they differ in the number of methyl groups bound to the aromatic ring (Nanditha and Prabhasankar 2009). The antioxidant activity of these homologs varies with the degree of hindrance and temperature. α-Tocopherol is one of the antioxidants most used and its biological activity is twice that of β and γ homologs and 100 times that of the δ homolog (Hix and others 1997). The use of tocopherols is limited to

fats, oils, and fat-containing foods. The properties of tocopherols are maintained in baked and fried products.

Quilez and others (2006) have carried out a sensory evaluation of two bakery products: croissants and magdalenas (Spanish muffins). They compared the same products with different added antioxidants such as phytosterol esters, α-tocopherol, and β-carotene. The phytosterol esters, α-tocopherol and β-carotene, were particularly suitable for inclusion in bakery products as functional ingredients and they did not affect the appearance or taste of the end product (Quílez and others 2006).

Park and others (1997) evaluated the effect of different ingredients with different antioxidants on bread characteristics. A mixture of wheat and psyllium husk fibers were substituted for flour, and the protein in the blend was restored by incorporating vital wheat gluten. After adding sodium stearoyl 2-lactylate, the blend was fortified with a combination of fat-coated ascorbic acid, protein-encased β-carotene, and cold-water-dispersible all-rac-α-tocopheryl acetate at levels of active material. The authors observed that the addition of these fiber ingredients increased dough absorption by about 25% and mixing time by 50%. The fiber and antioxidant bread showed a 10% reduction in loaf volume and a somewhat inferior crumb grain with an off-color caused by small, black specks on a dark gray background (Park and others 1997).

Phenolic compounds

Phenolic compounds are one of the main classes of primary antioxidants with a large range of structures and functions. Normally, these antioxidants have an aromatic ring bearing one or more hydroxyl substituent (Balasundram and others 2006). Phenolic compounds such as flavonoids, phenolic acids and phenolic diterpenes are responsible for antioxidative effect on a large range of food applications. The antioxidant activity of these compounds is mainly due to their redox properties, which can play an important role in absorbing and neutralizing free radicals (Javanmardi and others 2003). Flavonoids constitute the largest group of plant phenolics and are low molecular weight compounds. Variations in substitution patterns to heterocyclic ring result in the major flavonoid classes, i.e., flavonols, flavones, flavanones, flavanols, isoflavones, flavanonols, and anthocyanidins (Balasundram and others 2006).

Bassama and others (2010) evaluated the capacity of some natural antioxidant extracts to reduce acrylamide formation during the Maillard reaction in the baking process. The effect of pure antioxidant molecules on the net amount of acrylamide was investigated in an equimolar asparagine–glucose system during heating. Cinnamic acid and six phenolic compounds (gallic, ferulic, coumaric, caffeic acids, catechin, and epicatechin), displaying different antioxidant capacities, were added to the model system. The results indicated that the tested compounds did not reduce the net amount of acrylamide and a slight but significant promoting effect was observed for ferulic acid. An increase of antioxidant activity was also noticed during heating of the model solution spiked with caffeic acid, but the acrylamide level was not affected (Bassama and others 2010).

Carotenoids

Carotenoids are one of the most important classes of plant pigments that can prevent photo-oxidation and can be used as antioxidants in food products.

β-Carotene is one of the most frequently used carotenoids in food products. It has 8 isopropene units, which contain 40 carbon atoms and 2 rings at the end of its conjugated double bond chain. β-Carotene is a retinol precursor with a high conversion rate and provides a substantial proportion of vitamin A in the human diet (Silva and others 2011). For these reasons, there is a strong interest in using β-carotene and other carotenoids as functional ingredients in food products. This antioxidant action is limited, however, to low oxygen partial pressures (< 150 mm Hg), and at higher oxygen pressures, β-carotene may become prooxidant. β-Carotene is insoluble in water and soluble in fats and oils (André, and others 2010).

Hidalgo and others (2010) evaluated the loss of carotenoids content during the production of bread, water biscuits and pasta.. These authors observed that the total carotenoids content decreased throughout the processing stages. For bread and water biscuits, kneading led to limited degradation (on average, 15% and 12%, respectively), bread leavening had almost negligible effects (3%), while baking had a marked influence on loss of carotenoids in bread crust and water biscuits (29% and 19%, respectively) but not in bread crumb (3%). Overall, manufacturing led to average carotenoid losses of 21%, 47%, 31%, and 49% for bread crumb, bread crust, water biscuits, and pasta, respectively (Hidalgo and others 2010).

Brufau and others (2004) analyzed the effect of the consumption of croissants and magdalenas (Spanish muffins), enriched with sterol esters, α-tocopherol, and β-carotene, on plasma lipid peroxidation. Thiobarbituric acid and conjugated dienes were used as markers of lipid peroxidation. This study was carried out on a population without changes to their diet or lifestyle, and based on a randomized, double-blind, controlled repeated measures design. The treatment had a positive effect on TBA value for control group and that given to experimental group has negative effect. Also TBA was found to be significantly correlated with high-density lipoprotein-, low-density lipoprotein-cholesterol, and α-tocopherol, both before and after treatment, but TBA was only significantly correlated with β-carotene before treatment (Brufau and others 2004).

Gallates

Gallic acid esters, or gallates, are distributed in nature as a component of tannins and occur freely in tea and pomegranates. They are effective antioxidants as well as synergists for other antioxidants. They are soluble in water and virtually insoluble in fats. The main gallates used are propyl gallate, octyl gallate, and dodecyl gallate, which differ from each other in the length of their side chains (García-Melgares and others 2007). Sometimes the incorporation of 0.05% dodecyl gallate (calculated on the fat) has a favorable influence on the flavor of bakery products (Nanditha and Prabhasankar 2009).

Minerals and salts

Minerals are inorganic elements required by human body functions such as enzymatic reactions, bone mineralization, as well as the protection of cells and lipids in biological membranes. Their absence or deficiency – especially of iron, calcium, and zinc – have a relevant negative effect on human health and may result in diseases of the immune system, iron deficiency anemia, rickets, osteoporosis, and others. So, to maintain mineral balance, it is necessary to intake the correct amount of minerals that are available to be absorbed (Reykdal and others 2011).

Minerals are present in most food systems. Iron, calcium, and zinc are present in cereal grains (1.5–2.5%). Bread and bakery products made with cereal flours are a staple food in many countries and are therefore of global importance in international nutrition. However, most of the cereal grain (1–4%) has a low mineral bioavailability. This is because of the presence of endogenous phytase, an enzyme present in cereal grains capable of liberating covalently bound phosphate groups from the inositol ring, thus decreasing or eliminating the antinutritional effect of phytic acid (Gobbetti and others 2005). These enzymes act by hydrolyzing phytic acid into lower myo-inositol phosphate esters that have a lower capacity to bind minerals (Leenhardt and others 2004). Reduction of phytate content during bakery product processing depends on various factors such as phytase activity, degree of flour extraction, dough pH, and the presence of calcium salts. Therefore, the ingredients used in different bakery products may have different effects on mineral bioavailability.

Frontela and others (2011) evaluated the effect of fermentation and baking on the phytate content of different bakery products. Mineral availability in bakery products during processing was investigated by measuring solubility and dialysis, as well as the mineral uptake and transport by Caco-2 cells after in vitro digestion. Raw materials showed the highest amount of phytate, causing an important effect on the stage of processing. The solubility and dialyzability of iron increased with fermentation, while calcium and zinc showed a high variability depending on the product analyzed. These authors concluded that in vitro mineral availability of bakery products is influenced by the stage of processing and the ingredients used (Frontela and others 2011).

Calcium, iron, and selenium are of special concern since the intake of these elements might be limited and below the recommended intake in certain groups of the population, while the high intake of sodium in relation to potassium is a serious health concern in other groups. While variation in major mineral (Ca, K, Mg, Na, and P) content of foods is mainly determined by food processing and fortification, environmental conditions may greatly affect selenium and mercury in foods (Reykdal and others 2011).

Vitamins

The inclusion of vitamins in bakery products happens normally due their presence in some of the normal ingredients. Several studies have been made on the presence and distribution of vitamins in the ingredients of bakery products. A great variety of B vitamins (e.g., thiamine, riboflavin, pyridoxine, niacin, pantothenic acid, biotin, and folates) are found in wheat and differences in the amount of vitamin B documented have been related to the variety, location, soil type, and year (Batifoulier and others 2006). The processing of ingredients and bakery products are also factors that can affect vitamin B concentrations (Batifoulier and others 2006).

Fortification with vitamin D3 has only been carried out recently. Natri and others (2006) added vitamin D3 in form of cholecalciferol to bread (low-fiber wheat and high-fiber rye breads) and its stability, concentration added, dispersion, and bioavailability were studied. The vitamin was well dispersed in the breads and was stable. The bioavailability studies showed that fortified breads are a safe and feasible way to improve vitamin D nutrition (Natri and others 2006).

Alleged health benefits of functional ingredients

The awareness of a healthy lifestyle is increasing among consumers, who understand that deficient nutrition is linked to many health problems. Nowadays, the bakery industry seeks to improve the health attributes of their food products with functional ingredients that in some way can lead to health benefits. However, these added ingredients may not improve handling properties or flavor profiles, so a full study of their impact on bakery products and a high investment is needed.

The consumption of bakery products all over the world gives these food products an important position in nutrition. Besides macronutrients (e.g., starch and dietary fiber), micronutrients (e.g., antioxidants and minerals) are also present in the ingredients for making bakery products. Several factors affect the bioactivity and bioavailability of these nutrients, such as processing and interaction with others ingredients. Industrial and scientific communities have studied the effects of several factors that could influence the capacity, not only of existing nutrients but also of the fortification of some products, to add new functionalities (Dewettinck and others 2008; Kadam and Prabhasankar 2010).

Starch is undoubtedly one of the most consumed polysaccharides in the human diet as it is one of the main constituents of bakery products. Moreover, starch-based foods are digested at different rates due to the glucose and insulin responses that they induce. Consequently, bakery products lead to high glycemic values, and there are strong indications that the large amount of rapidly available glucose derived from starch and free sugars in the diet lead to periodic elevated plasma glucose and insulin concentrations that are unfavorable to health in many contexts, including diabetes and coronary heart disease. Low starch digestibility ingredients have used recently as a way to reduce the glycemic index and the health problems associated with high values of sugar absorption by developing low glycemic index diets for the prevention and treatment of diseases such as diabetes (Autio and others 2004). Low-fiber diets have been associated with atherosclerosis, coronary heart disease, and colon cancer, so increasing fiber in the human diet is one of the ways found to reduce the incidence of these diseases (Sanz-Penella and others 2009). Several studies have shown that resistant starch (RS) as a dietary fiber can improve bowel function, regulate blood sugar, and reduce calories, and can also be used to improve cholesterol metabolism and reduce the risk of colon cancer (Hong and Yoo 2012).

Non-starch polysaccharides and dietary fibers can be used as the functional ingredients in these products (Angioloni and Collar 2011). The consumption of dietary fiber is known to have a positive influence on several aspects of health, such as reducing the risk of colon cancer, constipation, hypercholesterolemia, obesity, diabetes, and it can be used as a laxative (Brummer and Cui 2005; Sivam and others 2013)

The use of composite and wheatless flours (gluten-free) instead of wheat flour for bread making is a very recent practise that aims to develop gluten-free products. Nowadays, the high incidence of celiac disease (gluten intolerance disease) has led food scientists to search for alternatives to a diet free of these allergens, creating gluten-free products (Shittu and others 2009). The supplementation of gluten-free bread dough with additives is difficult due its weak structure. A solution for this problem is the introduction of ingredients rich in dietary fiber. The nutritional value of food products containing barley depends on the level of

supplementation as well as on the type of tissue or milling fraction of barley grain used. β-Glucans one of the major fiber constituents in barley recognized by the FDA to reduce the risk of coronary heart diseases (FDA 2005). Other of the fiber components of barley is arabinoxylans (AX) that can be used to reduce serum cholesterol and improve the adsorption of calcium and magnesium (Izydorczyk and others 2008).

Fructo-oligosaccharides (FOS), AXOS, and inulin can bring health benefits if consumed on a regular basis. The health benefits include increased mineral absorption and improved immune response and although there is mounting evidence that prebiotics play a role in colorectal cancer prevention, their role in satiety and weight management is still being investigated (Damen and others 2012; Morris and Morris 2012).

Bakery products with high fiber content, however, could contain high phytate levels (leading to low mineral absorption). Enzymatic phytate degradation depends on many factors (e.g., fermentation time, temperature, pH, water content of dough, flour extraction rate, starter culture, mineral content, leavening agent, and the bread-making process). If high-fiber bakery products are produced, new strategies are needed to eliminate phytate from the food. This can be achieved by the addition of exogenous phytate-degrading enzymes, changes in breeding, genetic engineering, or changes in food processing (Sanz-Penella and others 2009).

Probiotics have been proposed for various treatments of human intestinal barrier dysfunctions such as lactose intolerance, acute gastroenteritis, food allergy, atopic dermatitis, Crohn's disease, rheumatoid arthritis, and colon cancer (Anal and Singh 2007; Burgain and others 2011). They have already been incorporated in bakery products; however, further studies are needed to evaluate their viability after baking.

Some of the problems with diets deficient in vitamins and minerals are associated with hematopoiesis (e.g., iron, vitamin B12, and folic acid), bone health (e.g., zinc and vitamin D), immune functions (e.g., vitamins A, E, and B6), cognitive functions (e.g., iron, zinc, vitamins E, C, and B), cardiovascular health (e.g., vitamins B6, B12, and folic acid), and insulin action (e.g., chromium, zinc, vitamins C and E). A great variety of B vitamins (e.g., thiamine, riboflavin, pyridoxine, niacin, pantothenic acid, biotin, and folates) are found in wheat. These molecules are water soluble and play an important role in metabolism, particularly of carbohydrates (thiamine), proteins, and fats (riboflavin and pyridoxine). However, sometimes the human daily intake is not sufficient. Solutions include fortification, the use of ingredients with high values of vitamins, and optimization of the food processing techniques to provide a diet rich in folates within the range indicated as protective for human health (Jagerstada and others 2005).

Conclusions and future perspectives

The increased interest in functional foods is a result of the increase in the cost of health maintenance, given the increase of life expectancy, and also the interest of older people in extending their quality of life.

The ingredients used in the manufacture of bakery products have many and diverse functional properties, and each ingredient can perform more than one function in a particular product. These ingredients are used to adapt the properties of the final product through the stabilization and distribution of air, improvement of the nutritional quality of the product, its taste and color, and an increase in shelf-life.

However, several aspects of the process and the bioavailability of the functional ingredients have not yet been assessed. Research is required in the following areas:

- study of the influence of the thermal process on the functionality of active ingredients;
- use of new technologies such as microencapsulation to protect bioactive ingredients during the baking process;
- study of the bioavailability and physiological effects (synergistic and antagonistic) of a combination of bioactive ingredients present in the baking product.

The market for functional foods and ingredients is growing and represents innovation opportunities for agro-food industries, with great potential to promote competitiveness.

Acknowledgments

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26
Rheology of Bread and Other Bakery Products

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Introduction

When wheat flour is kneaded with water, the presence of gluten in dough gives rise to complex behaviors which are critical to the creation of the final product structure. The most significant of these are known rheologically as viscoelasticity, strain dependency, and history dependency characteristics. These can be characterized and understood through rheological testing where deformation by compression, tension or flow tests are conducted through controlled applications of stress and strain on dough. The rheological behavior of dough has drawn a great amount of attention amongst bakers and researchers as these properties are intimately linked to baking performance and bread quality. More generally, rheology is relevant to the wide range of bakery products, including cakes where the right consistency of mixed batter is needed to produce a well-risen cake.

A full presentation of the rheology of bread doughs and other bakery products would merit a book of its own. Here a summary is presented of the two main themes: the role of rheology in baking performance and quality, and rheological measurements for bakery products. Emphasis is given to the role of rheology in processing and the creation of structure, rather than the properties of the final products themselves, since experience has shown these to be the most important phenomena.

Role of rheology in baking performance and quality

Most studies on dough rheology are conducted through dough mixing studies where good correlations with baking qualities, particularly loaf volume, can be obtained (El-Dash 1978; Skeggs and Kingswood 1981; He and Hoseney 1991; Kenny and others 1999; Suchy and others 2000; Autio and others 2001; Dobraszczyk 2004; Sliwinski and others 2004; Stojceska and others 2005; van Vliet 2008). In the proofing stage, as dough expands, rheological changes continue and may be seen as the extension and growth from the earlier characters set during the mixing stage (Chin and others 2009; Cardoba 2010). In more liquid dough systems, including those of cake batters, rheology (sometimes just viscosity) is measured and linked to cake quality parameters such as volume and texture (Huang and Tseng 2007; Angioloni and Collar 2008; Turabi and others 2008; Nakamura and others 2010).

Physical and rheological changes in bread dough during mixing and proofing

The major change in dough rheology during mixing derives from the biochemical and physical changes of dough during a mixing process. A Farinogram charting the change in consistency of dough by measuring the torque exerted during a mixing process is shown in Figure 26.1. Mixing actions impart both elongation and shear to the dough. The strains incurred could be up to 500 000% over the course of mixing and these have a major effect on the molecular arrangement of the gluten, significantly contributing to the development of the dough. Shear rates during a mechanical dough development process are in the range of 10–100 s^{-1} (Menjivar 1989). The high shear rate in the mixer removes the outer layer of flour particles as they become hydrated and exposes a new surface for hydration whilst a lumpy mass of dough is formed (Figure 26.1a-I). The dough gradually becomes coherent and exhibits elasticity, plasticity and memory as well as viscous properties. Continuing mixing reduces the tendency of dough sticking and produces a smooth surface with dough seen wound around the mixer. It stiffens as mixing proceeds and the viscous and elastic components increase up to a point of optimum consistency, known as peak development, when the torque on the mixer shaft or the power consumption of the motor is the greatest (Figure 26.1a-II). The dough looks silky and glossy at this stage. If mixing is continued, the consistency of the dough will decrease as mixing torque and power decrease. Dough elasticity decreases and dough becomes increasingly extensible or plastic (Figure 26.1a-III). If over-mixed, it becomes sticky and extensible.
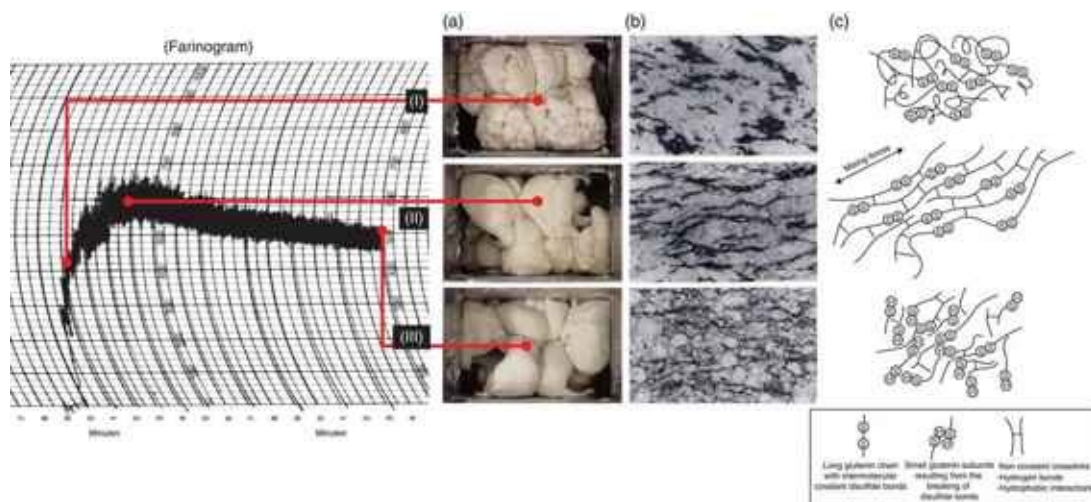
Figure 26.1 (a) Physical changes of dough in a Farinograph mixer at mixing time of (I) 1 minute, (II) 4 minutes and (III) 15 minutes corresponding to (b) micrographs and (c) molecular interpretations of gluten development of doughs at under-developed, optimally and over-developed stages. Picture 1b (From Moss 1974, *Cereal Science Today*, 19, 557–561. Reproduced with permission of Elsevier). Picture 1c (From Letang and others 1999, *J Food Eng*, 41,121–132. Reproduced with permission of Elsevier).

Molecularly, the physical changes that appear in dough during the course of mixing result from the formation of a gluten network, a unique composition and interaction of hydrated gliadins and glutenins. The presence of water provides a medium for molecular interactions and reactions between proteins in flour. Both chemical and physical processes occur and work in tandem. Ascorbic acid is a common additive oxidant (often known as improvers) which accelerates the development process, but itself requires oxygen through the dough aeration process. In the initial stage of mixing, when the dough is a lumpy mass, the proteins formed are swollen. They are compact isolated masses with adhering starch granules. These glutenin molecules are distributed randomly (Figure 26.1b-I and c-I). As mixing progresses, the protein starts to become inter-connected; the protein masses are stretched into continuous sheets that support starch granules (Figure 26.1b-II and c-II). The glutenin molecules are stretched and extended into strands forming films. The mixing process helps to align the gluten molecules to build a network consisting of unbranched glutenin molecules. The alignment of glutenin molecules leads to a large number of the non-covalent bonds such as the hydrogen bonds, hydrophobic bonds and chain entanglement. The unbranched glutenin molecules have disulfide cross-links within the chains and non-covalent cross-links between the chains. At optimum mixing, Bernardin and Kasarda (1973) described the structure of wetted protein sheets in laminar disposition as protein fibrils, a structure which refers to a large ratio of length to width. Further mixing causes film perforation and disruption. The protein aggregate is broken down and glutenin molecules depolymerize (Figure 26.1b-III and c-III). Mechanical fission of the polypeptide chains occurs and the average molecular weight of protein decreases (Danno and Hoseney 1982b). Hoseney (1985) referred to this as cleaving of disulfide bonds. This protein depolymerization theory is supported by the markedly increased amount of protein extracted from dough when mixed excessively (Tsen, 1967; Tanaka and Bushuk, 1973; Danno and Hoseney 1982a, 1982b; Hoseney, 1985). These molecular changes of protein molecules during mixing are the principal cause of the physical and rheological changes in dough during mixing.

The rheological properties of the gluten network lends dough the ability to entrap gas bubbles

and subsequently form a stable foam structure (Baker 1941; Baker and Mize 1941). These trapped gas bubbles grow as yeast evolves carbon dioxide in proofing and then as gases expand and water vapor is evolved in baking, making doughs expand in volume with time. At the microstructure level of dough, the presence of starch granules, insoluble proteins (gluten) and gas bubbles as dispersed objects in the continuous phase of soluble protein have also been alleged to affect rheological properties of dough. With starch granules making about 60% of the liquid dough phase volume (Bloksma 1990) and gas bubbles of 5–10% at normal atmospheric mixing (Campbell and Mougeot 1999), the starch content in the dough contributes to dough stiffness (Bloksma 1981) while aeration reduces the failure stress and strain in doughs (Chin and others 2005). Proofing doughs with relatively higher air contents than mixed doughs has shown rheological weakness in uniaxial elongation test (Newberry and others 2002).

Physical and rheological changes in cake batter during processing

The effect of processing on rheological characteristics of cake batters has received relatively less attention compared to bread doughs (Meza and others 2011). However, the physical and structural changes in cake batter processing are as important as they also govern the performance and quality of the final cake product (Huang and Tseng 2007; Angioloni and Collar 2008; Turabi and others 2008; Nakamura and others 2010). The quantitative assessment of microstructure development of cake batter is more to measuring its foam rheology where simple shear tests are conducted to obtain apparent viscosity and viscoelasticity. As foam suggests air incorporation and holding capacity, the generation of cake batter through mixing is typically an aeration process of a water-based mixture combining wheat flour, sugar, egg, fat, leavening agents, salt, water, and milk in appropriate proportions to form a continuous fat–water emulsion that can sustain insoluble materials and gas bubbles. In cake batters, the development of a gluten network is limited compared to dough due to their high sugar and fat content. Instead of gluten, proteins such as egg white and whey protein isolates are used as the foam stabilization agents during a whipping process. Gas bubbles become entrained in the liquid albumen or continuous phase as mixing of other ingredients take place producing a thick liquid with governing viscosity as the controlling factor of cake quality. A low batter viscosity will not entrap sufficient air during mixing and retain the bubbles formed because the liberation of gas during baking leads to a small cake volume, while a high viscosity will prevent bubbles from rising in retrospect of buoyancy force.

Rheological measurements for bakery products

The instrumental measurements of rheology for bakery products are broadly classified into the fundamental or empirical approach. The fundamental methods provide absolute values of well-defined physical properties and measured parameters. They are useful for describing the structure–property relationship and for performing process and engineering calculations. The empirical methods may be termed as conventional as they are more descriptive and imitative. Empirical measurements can be simpler and faster, although they are more vague about what is being measured. Rheologists claim that "with the empirical methods, they do not know what is being measured but it works, whereas with the fundamental methods, they know exactly what they are measuring, but it doesn't work" (Weipert 2006). Despite being claimed as having little relevance to practical baking results, the fundamental methods provide better defined experimental conditions of stress and strain that allow interpretations of results in fundamental units for design and calculations purposes (Hibberd and Parker 1975; Muller 1975). The empirical methods of measuring dough rheology have been used extensively for flour characterization and quality control, giving useful information to the relevant and experienced.

Understanding basic rheology

That the deformation of solids can be exerted either by a normal force or stress that acts perpendicular to the face of the material, or shear stresses that act tangentially to the face of the cube resulting in elongation and shear deformation is illustrated in Figure 26.2. In an ideal elastic solid, the original shape is regained instantaneously when the stress is removed. A small deformation test is such that the applied stress is small and the solids are able to regain their original shape. A large deformation test is when the applied stress exceeds the yield value, the original shape is not regained after the removal of the applied stress and it involves structural breakdown or macroscopic fracture.
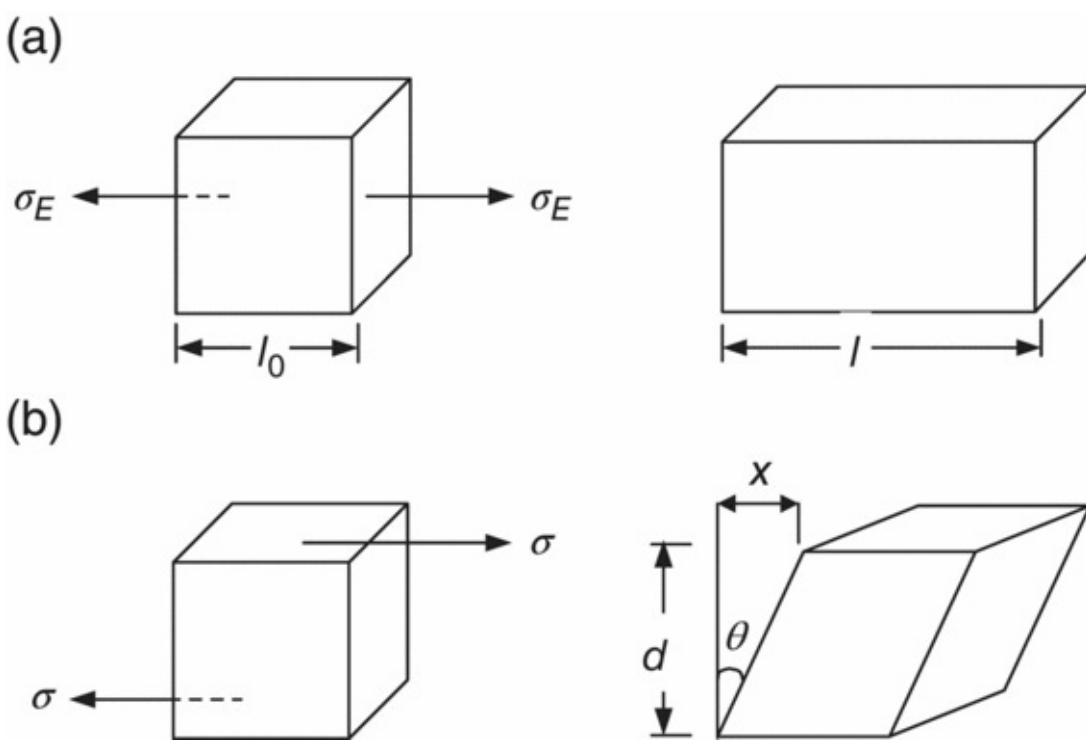
Figure 26.2 Deformation in solids by (a) normal stress in an elongation test and (b) shear stress in a shear test.

Equation 26.1 describes the stress and strain relationship of a normal and shear test where σ_E is the elongational or normal stress (N), ε is the elongational strain, and E is Young's modulus (N) describing the strength of the material. The elongational strain here refers to the engineering or Cauchy strain where it is a simple ratio of length changes with original length. In most strain calculations of dough, the true or Hencky strain is calculated as logarithm l/l_o to normalize the stress or strain as the change in dimensions with stresses and strains is less uniform and unpredictable compared to stiffer materials. Equation 26.2 describes a shear deformation with shear parameters consisting shear stress, σ (N), shear strain, γ and shear modulus, G (N). Equations 26.3 and 26.4 describe the behavior of stress with strain rate, $\dot{\varepsilon}\,(s^{-1})$, and shear rates, $\dot{\gamma}\,(s^{-1})$, respectively for liquid deformation. The proportionality constant between shear stress and shear rate is known as the viscosity, η (Pa s) and η_E (Pa s) is the extensional viscosity.

$$\sigma_E = E\varepsilon = E\left(\frac{l-l_0}{l_0}\right) \tag{26.1}$$

$$\sigma = G\gamma = G\left(\frac{x}{d}\right) = G\tan\theta \tag{26.2}$$

$$\sigma_E = \eta_E\dot{\varepsilon} \tag{26.3}$$

$$\sigma = \eta\dot{\gamma} \tag{26.4}$$

The viscosity of an ideal liquid (Newtonian) is constant, independent of shear rate. The apparent viscosity of a non-Newtonian liquid is a function of shear rate, $\eta_{app} = f(\dot{\gamma})$. Figure

26.3 shows the classical presentation of liquid types using the shear stress-shear rate graph. Bread doughs and cake batters posses shear thinning (no. 2) characteristics. The general power law (Equation 26.5) is commonly used to describe these liquid behaviors through rheological parameters of consistency coefficient, K (Pa s^n) and power law index, n. While the stresses and strains are applied through various test methods, the time scale of deformation and the flow history are also very important for many non-Newtonian food materials including doughs. The thixotropic model describes a material where its apparent viscosity decreases with time of flow while in rheopectic (antithixotropic) material, its apparent viscosity increases with time of flow. Dough, in particular is known to be thixotropic as it is gel-like at rest but fluid when agitated (Smith and others 1970). In studying the ageing of solid doughs, the stress relaxation test, an assessment of stress decrease with time when strain is held constant and the creep test, the assessment of strain increase with time when stress is held constant are useful.
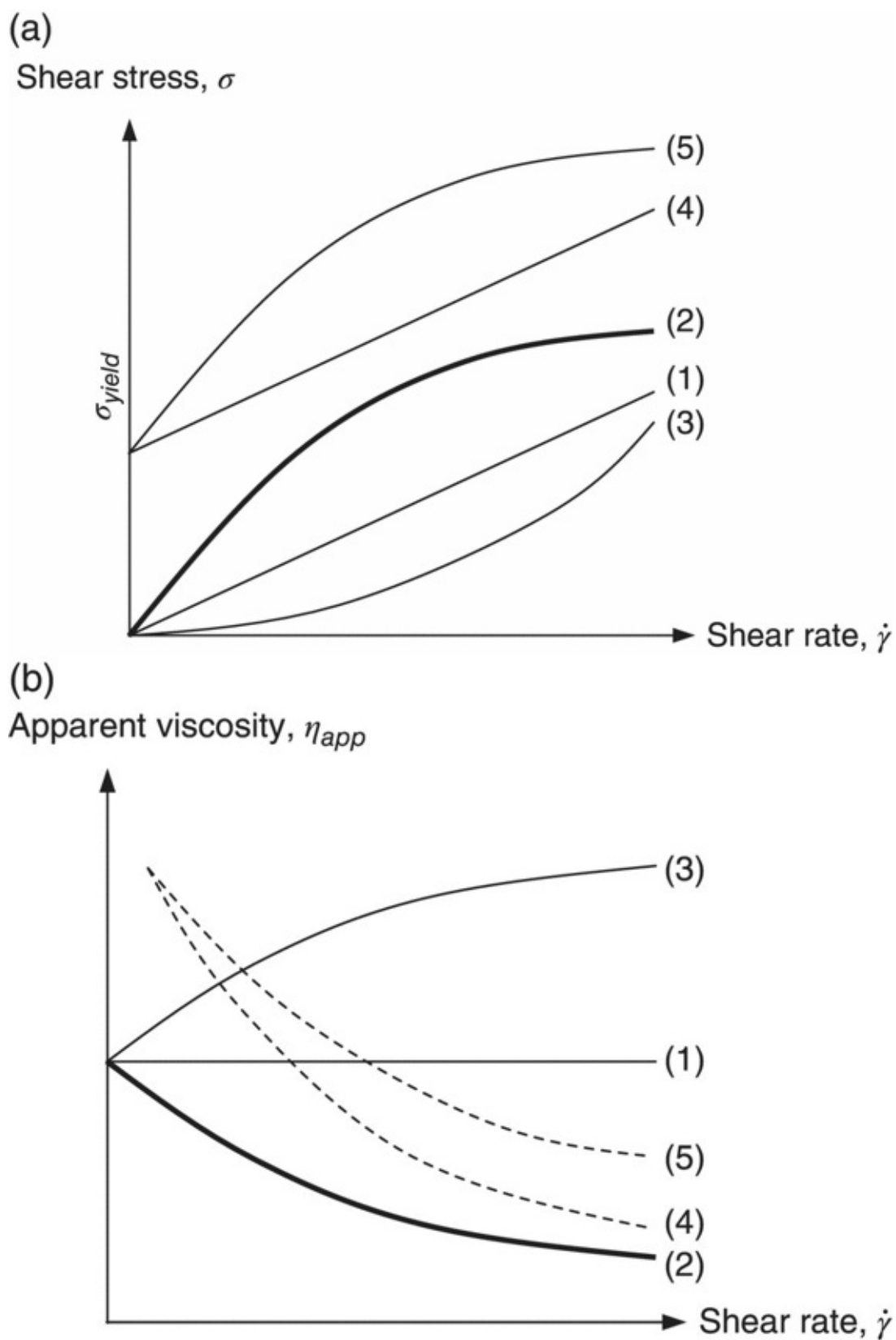
Figure 26.3 (a) Shear stress and (b) apparent viscosity as the function of shear rate for various liquid characters. (1) Newtonian liquid, (2) shear-thinning behaviour (pseudoplastic), (3) shear-thickening behaviour (dilatant), (4) Bingham liquid and (5) plastic.

$$\sigma = K\dot{\gamma}^n \tag{26.5}$$

Fundamental testing

In fundamental rheological testing of doughs, they are capable of performing tests under

defined conditions such as a fixed strain rate and the resultant deformation such as the strain and stress are measured or calculated. The rheometer is commonly used for small deformation. The more solid like sample such as dough is tested by a dynamic oscillatory shear test while more liquid samples undergo a flow test. Instruments that cause destruction to the sample (large deformation categories) include texture analyzers and universal testing machines.

The dynamic oscillatory shear measurements (DOSM) measure the kinetics of stress in samples involving strains of the order of 0.1–5% (Menjivar 1989). The type and geometry of a DOSM vary widely but the principles are the same regardless of the testing geometry. The parallel plate geometry testing mode is commonly used for measuring dough. A dough sample is placed between two parallel plates, one plate is fixed to a force transducer (stationary) and the other plate is oscillated (movable) at frequency, ω. As the movable plate oscillates at a sinusoidal strain, ($\gamma = \gamma_o \sin \omega t$) with an amplitude of γ_o, the dough responds with a sinusoidal stress, ($\sigma = \sigma_o \sin \omega t + \phi$) with amplitude of σ_o captured from the force transmitted through the sample or force acting over the sample area by the force transducer attached to the stationary plate. If the sample is completely elastic, the two curves peak together; there is no phase lag and the phase shift, ϕ in degree will be zero. If the sample is completely viscous, the two curves will be out of phase by 90°. The elastic component is accounted as the storage modulus, $\left(G' = \dfrac{\sigma_0}{\gamma_0} \cos \varnothing \right)$ and the viscous component is measured as the loss modulus $\left(G'' = \dfrac{\sigma_0}{\gamma_0} \sin \varnothing \right)$. In lay terms, G' is the part of the energy that is stored (elastic property) and G'' is the part that is lost (viscous property) during the test cycle. The ratio of complex stress and complex strain gives the complex modulus, G^*, which is made up of the storage modulus, G', and the loss modulus, G'' (Equation 26.6) (Faubion and others 1985; Hoseney 1998). The tan ϕ term, also the ratio of G''/G' is used as a simple index of the relative viscosity to elasticity of dough. The critical part of this test is that the contact between the oscillating plate and the dough sample must not slip. A typical viscoleastic plot of G' and G'' versus frequency is known as the mechanical spectrum of $G',G'' = f(\omega)$ (Figure 26.4).

$$G^* = \left(G' + iG'' \right) \tag{26.6}$$
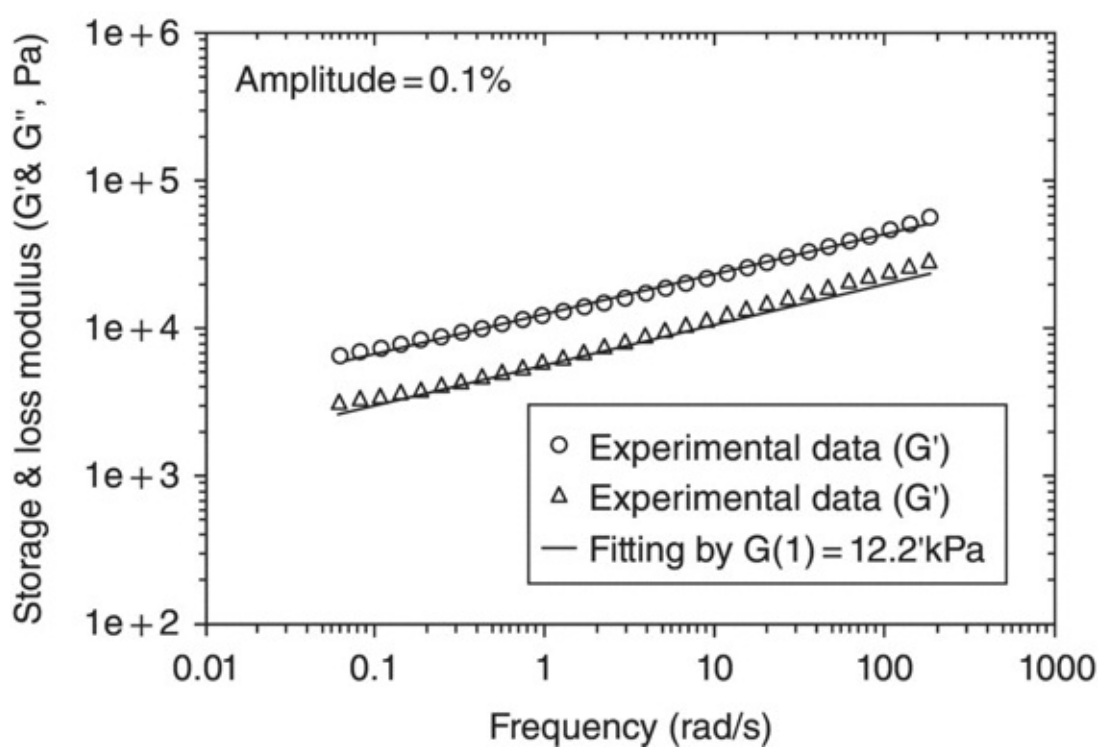
Figure 26.4 Mechanical spectrum of *G′* and *G″* of medium strength Australian dough at small strain of 0.1%. (From Tanner and others 2008, Journal of Non-Newtonian Fluid Mechanics, 148, 33–40. Reproduced with permission of Elsevier)

Besides oscillating the movable plate, the plate can also be rotated at a constant angular velocity that in turn gives rise to a constant shear rate at the plate edge. In such configuration, a sample of dough in the shape of a disk is loaded between the two plates and the lower plate is rotated. Torque is measured at the upper plate and shear stress is calculated at the plate edge. The total shear strain applied to the dough is calculated by multiplying the shear rate by the elapsed time in a constant shear rate experiment. The stress–strain diagram illustrated in Figure 26.5 is obtained and expressed in fundamental units. A similar concept of flow test using concentric cylinders is used when measuring more liquid samples. The shear stress created by the movement of a spindle connected to a torque transducer is accounted while it is set to a range of shear rates. A strain sweep or time sweep test is performed to determine the linear viscoelastic region so that testing conducted has a response within its reversible deformation.
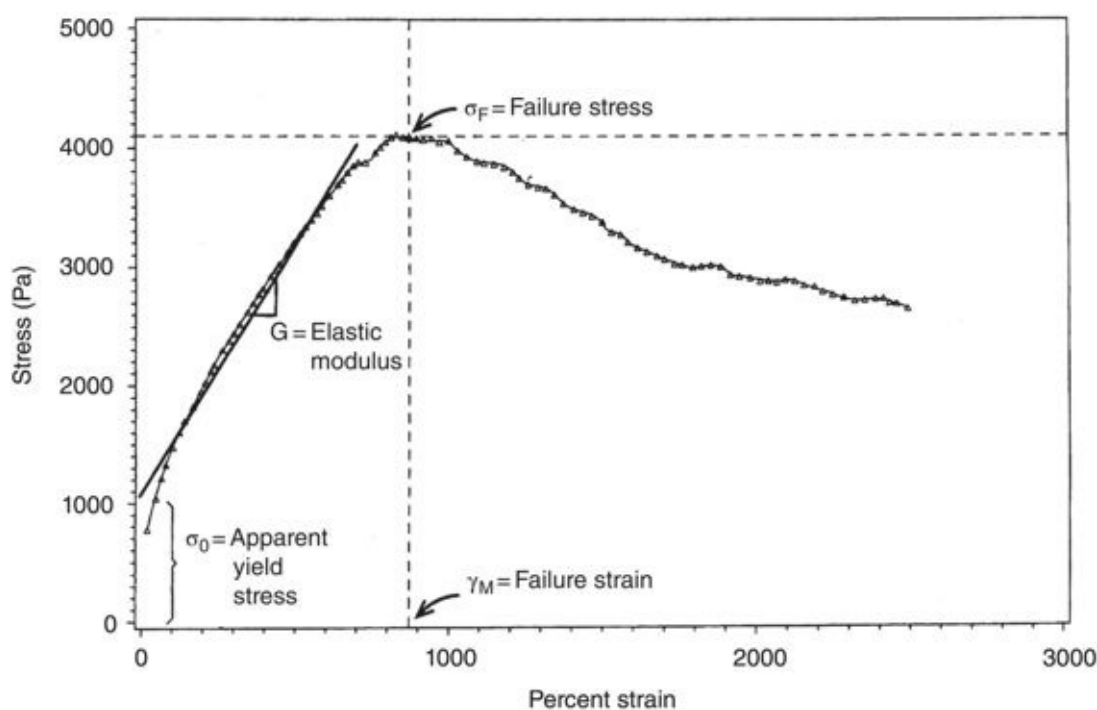
Figure 26.5 Representative of shear stress–strain diagram obtained with the plate–plate configuration at shear rate of 0.05 s^{-1} using Rheometrics Fluids Rheometer. (From Menjivar, 1989, Fundamental aspects of dough rheology. In: Faridi, H. A. and Faubion, J. M., editors. Dough Rheology and Baked Product Texture. NY., USA: Van Nostrand Reinhold. p. 1–28. Reproduced with permission of John Wiley & Sons).

These small deformation tests using oscillatory and flow movements are most common in assessing the fundamental mechanical characteristics of wheat flour dough. It is, however, claimed that there was no direct relationship for either the dynamic moduli or tan ϕ to loaf volume (Janssen and others 1996). Instead, the information obtained was complementary to biaxial extension, a type of large deformation test which is claimed to have better correlations with baking performance. The large deformation test requires a sample to be tested up to the point of failure where dough is compressed or extended. The texture analyzer, for example, is used for simple dough compression and tensile tests in uniaxial mode. The machine has an arm with a sensitive probe to detect the force applied versus distance or time when performing a compression or extension test. From the test geometry and principles of deformation, calculated stress versus strain graphs are plotted. These tests give a limited indication of dough's viscoelastic properties. Their adaptability to samples of different natures is good as they have specific attachments for dough tests such as the SMS/Keiffer Dough and Gluten Extensibility Rig for simple extension tests on small dough strips, the Dobraszczyk–Roberts (DR) Dough Inflation System for measuring biaxial extensional deformation of dough (Dobraszczyk 1997), and the SMS/Chen–Hoseney Dough Stickiness Rig which measures dough stickiness. The stress–strain curves derived from a uniaxial and biaxial extension dough test are shown in Figure 26.6 and Figure 26.7, respectively.

(a)
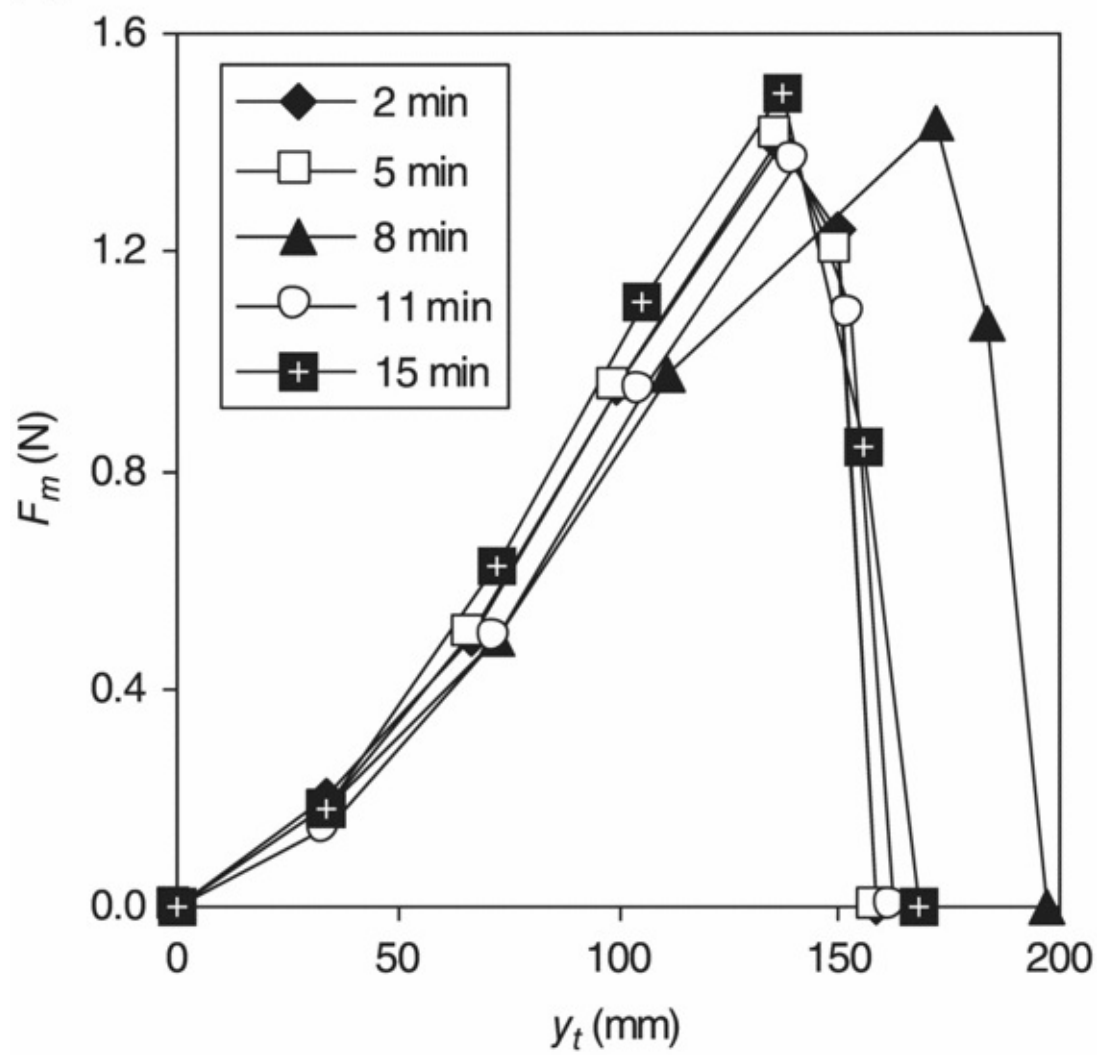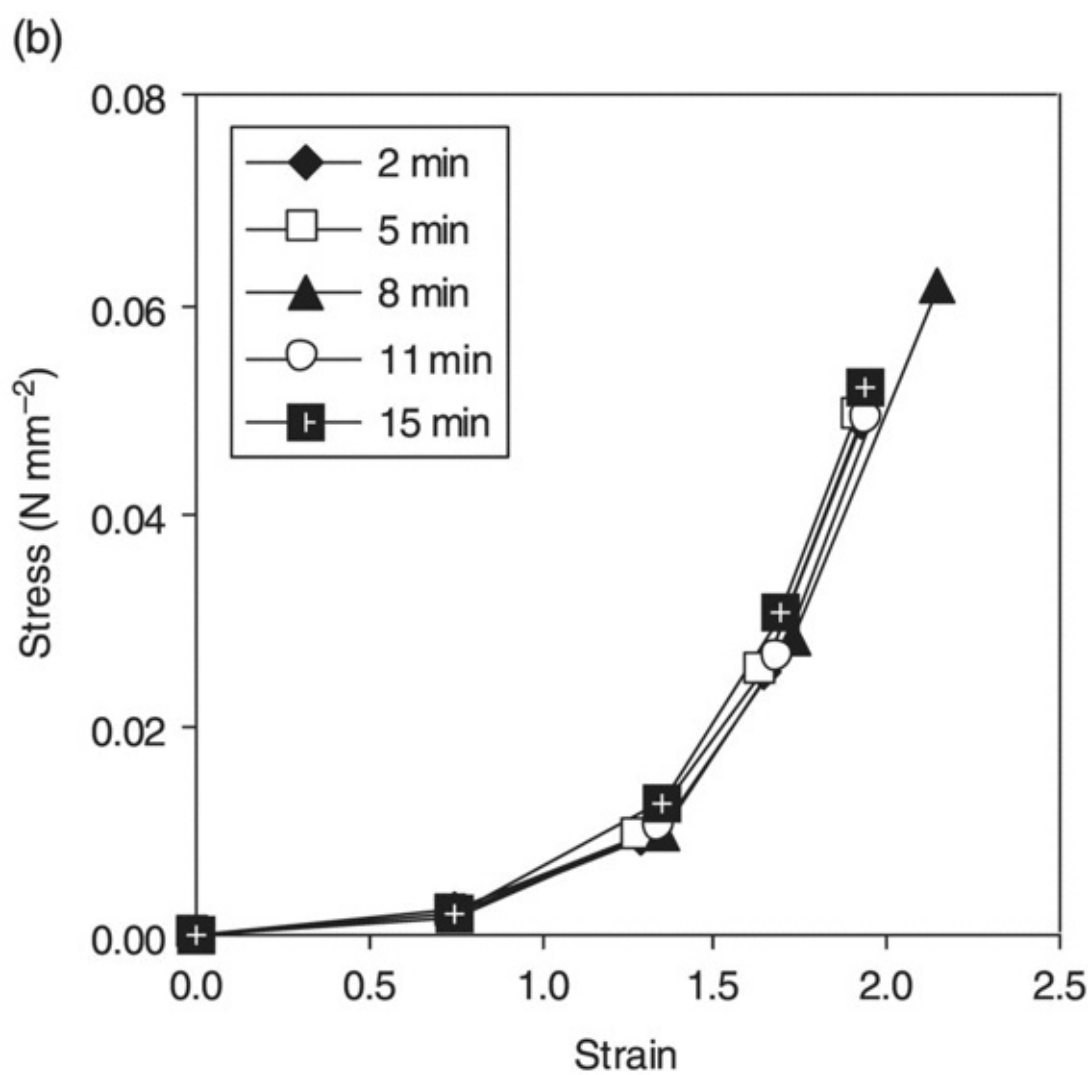
Figure 26.6 (a) Measured force-hook F_m displacement Y_t curves and (b) their corresponding stress versus strain plots for an uni-axial extension test of gluten from doughs mixed to various mixing times using strong flour (Diamond) using a universal testing machine. (From Abang Zaidel and others 2008, *J Food Eng*, 86, 549–556. Reproduced with permission of Elsevier).

(a)
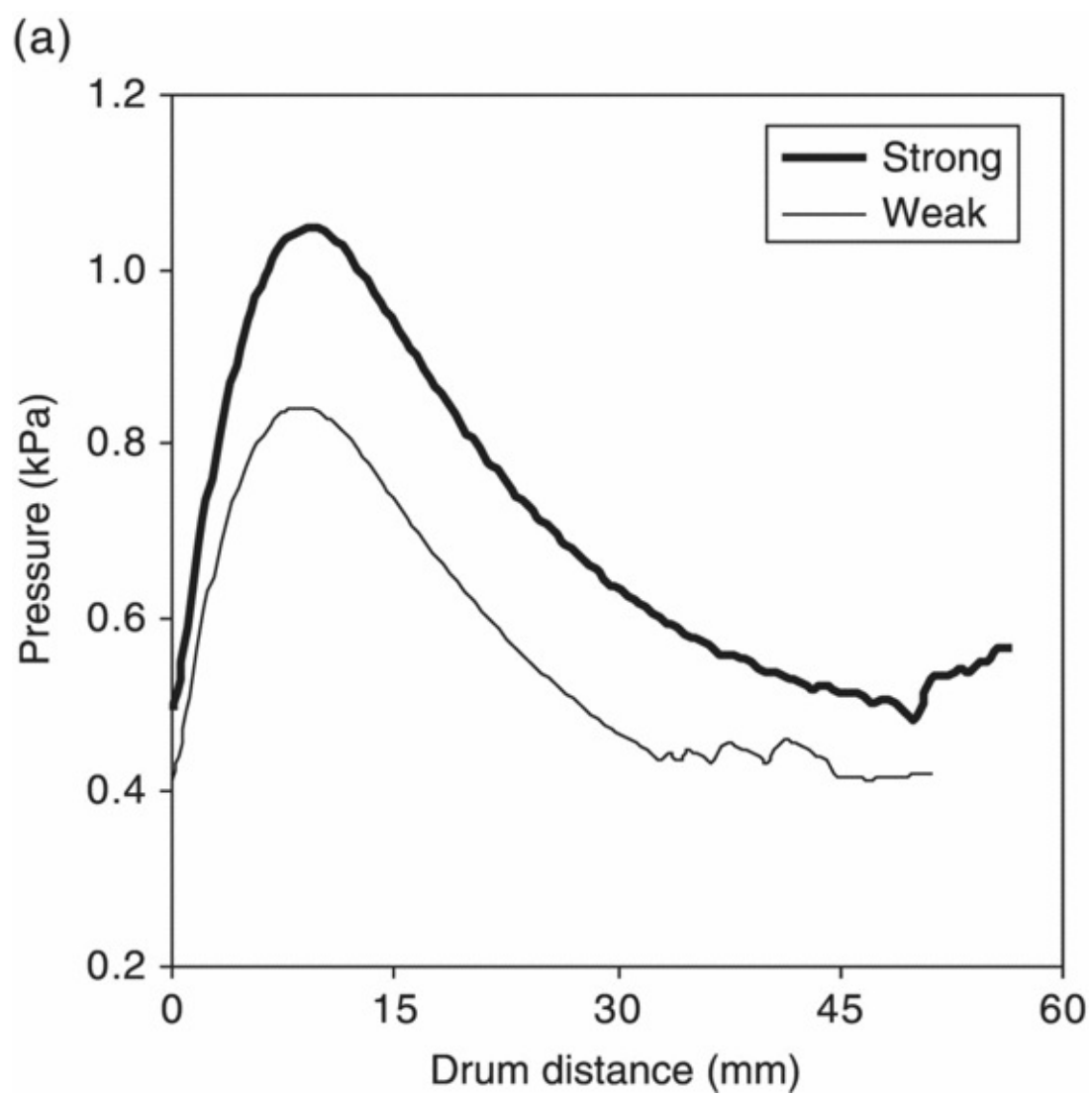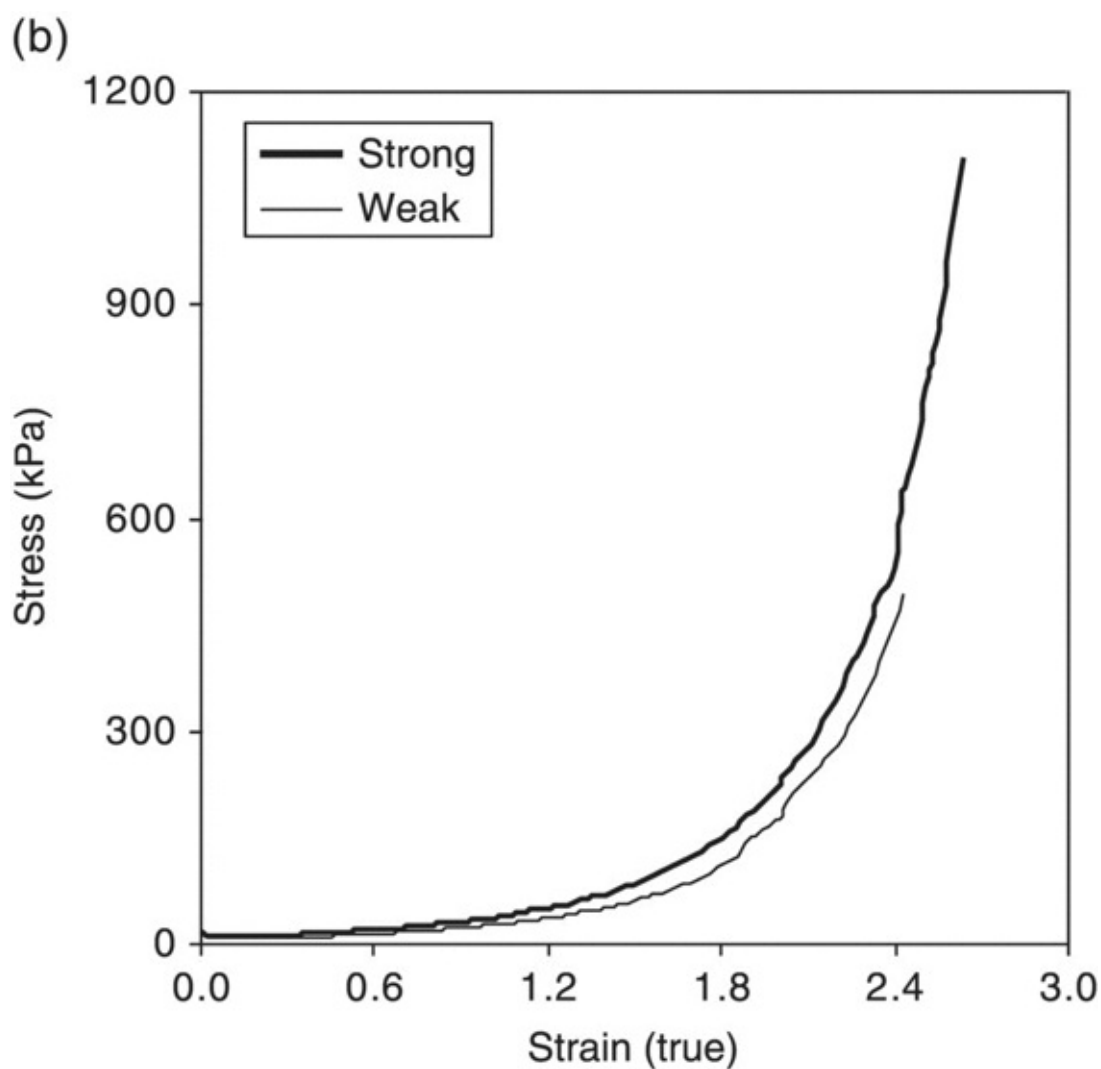
Figure 26.7 (a) Pressure versus drum distance plots of inflating dough bubble and (b) their corresponding stress versus strain plots for a biaxial extension test of dough for doughs mixed with strong flour (President White) and weak flour (Soft Patent) using a texture analyser. (From Chin and Campbell, 2005, *J Sci Food Agric*, 85, 2194–2202. Reproduced with permission of John Wiley & Sons).

Empirical testing for flour and dough

The empirical testing methods play a major role in measuring flour quality and evaluating dough properties. These instruments mainly characterize dough by simulating their behavior during mixing and proofing or through large deformation tests where the equipment is designed to acquire empirical data quantified in its own units. The main manufacturers of these empirical test machines are the Brabender Instruments Inc. from New Jersey, USA, Chopin Technologies from Villeneuve La Garenne, France and National Manufacturing Co. from Nebraska, USA. They each have compatible equipment of similar purpose and function. The rheological tests mainly follow the standard testing methods approved by the Association of Cereal Chemists (AACC) and International Association for Cereal Science and Technology (ICC).

Categorized lists of the equipment and their relevant approved standard tests are given in Table 26.1. The standard tests are important for enabling laboratories to compare their results using suitable conditions. In general, the Farinograph, Consistograph, and Mixograph are mixers that are designed to determine the quality of flour by recording the torque generated

during dough mixing. The recording mixers measure the resistance of dough against the mixer blades. The Extensograph and Alveograph measure the stretching behaviors of doughs. The Alveograph applies a three-dimensional extension of dough while the Extensograph measures uniaxial extension. In studying dough development and gas release during a proofing process, the Maturograph, Fermentograph, Oven-rise Recorder, Rheofermentometer or Risograph measure the production and retention of gas during a fermentation process and the maximum height reached by dough while recording the gas release during proofing. The Amylograph and Viscograph by Brabender are instruments that measure and record the gelatinization temperature and viscosity of starch and flour pastes.

Table 26.1 Categorized rheological testing equipment and their approved standard/method

Rheological testing equipment	Brabender	Standard/method no.[a]	Chopin	Standard/method no.[a]	National	Standard/method no.[a]
Recording mixer	Farinograph	ICC 115/1 AACC 54–21 ISO 5530–1	Consistograph Mixolab	ICC 171 AACC 54–50.01 ICC 173 AACC 54–60.01	Mixograph	AACC 40A
Stretch tester	Extensograph	ICC 114/1 AACC 54–10 ISO 5530–2	Alveograph	ICC 121 AACC 54–30.02	–	
Proofing recorder	Maturograph, Fermentograph Oven-rise recorder		Rheofermentometer	AACC 89–01.01	Risograph	AACC 01

[a] ICC, Standard Methods of the International Association for Cereal Science and Technology (ICC 1992–2011); AACC, International Approved Standard Methods for the American Association of Cereal Chemists (AACC 2000) ; ISO, International Organization for Standardization (ISO 2012–2013).

In studying some of the rheological parameters from these empirical tests, the Farinograph, being more familiar among millers and bakers, produces a Farinogram (Figure 26.1 and Figure 26.8) showing the amount of resistance (the torque) measured in Brabender units (BU) from zero (bottom) to 1000 (top) during mixing. The flour characteristic is determined by the flour water absorption level from the amount needed for the centre of the peak to fall onto the 500 BU line. Parameters which characterize the curve from the Farinogram are the arrival time, A which measures the rate of flour hydration; dough development or peak time, B which correlates with the mixing time; stability, C which is the duration at which consistency is ≥ 500; departure time, D which is the time for consistency to decrease below 500; mixing tolerance index (MTI) which is the vertical distance between the upper edge of the curve at the peak and five minutes later (about 20 units in this example). The MTI and stability are most often used to indicate flour strength. The relationship of these two parameters to flour quality and its types of products is given in Table 26.2. Strong doughs show an increasing consistency at the beginning of mixing and a gradual decrease on

reaching the maximum (high stability). A weak flour of low quality shows a rapid increase in consistency and a sharp decrease on reaching the maximum (low stability). In this empirical method, the term consistency is used vaguely and expressed in arbitrary Brabender units with no precise units of viscosity measurement. Kilborn and Tipples (1972) and Tipples and Kilborn (1977) have referred dough consistency term as energy requirement for dough development while Olewnik and Kulp (1984) referred dough consistency to stiffness when using the Farinograph.
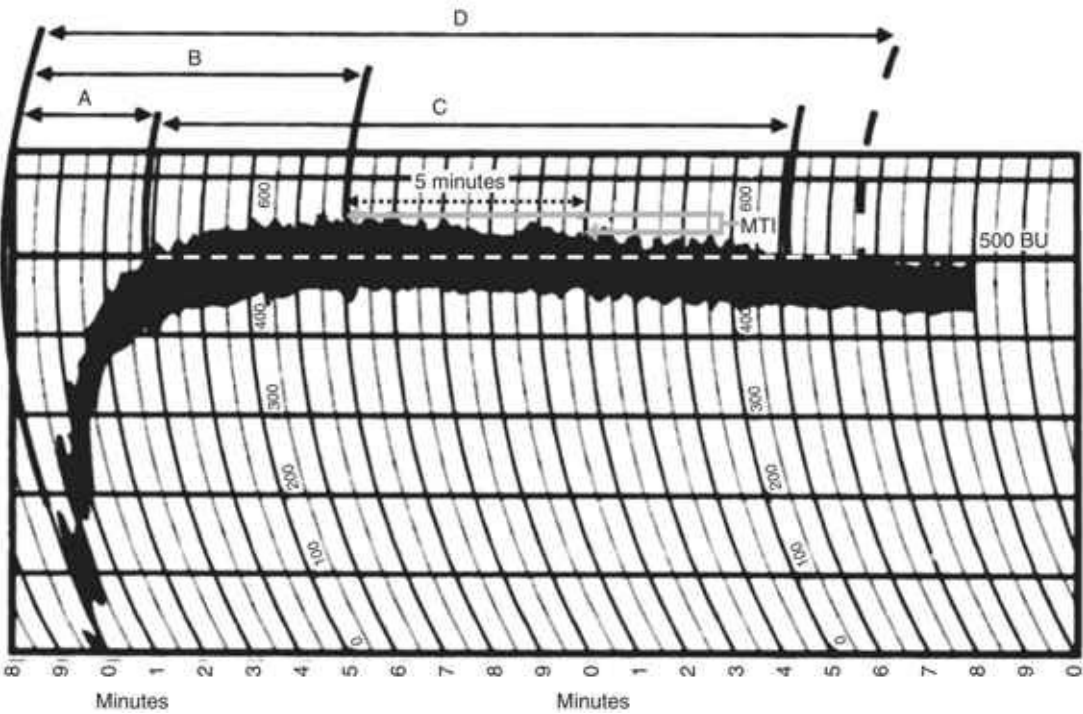
Figure 26.8 The Farinogram indicating rheological properties measured through its arrival time (A = 3 minutes), peak time (B = 7 minutes), stability (C = 13 minutes) and departure time (D = 17.5 minutes).

Table 26.2 The characteristics of mixing tolerance index (MTI) and stability of the Farinograph with flour quality and products

MTI (BU)	Stability (min)	Flour quality	Type of product
20	15–17	Strong	Hearth bread, pizza crust
20–40	10–13	Medium strength[a]	Pan bread, regular rolls
40–50	8–10	Mellow–good	Pan bread, tin bread, rolls with more spread, sweet goods dough, donut
50–70	5–7	Fair	Flat breads, baguettes, noodles
70–130	3–5	Poor	Crackers
>130	<3	Inferior	Cakes, cookies

[a] Also known as Standard Bakers

The Extensograph is a load extension instrument for empirical measurement of stress–strain relationships. Cylindrically molded mixed dough is clamped at both ends after a rest period

and stretched through its midpoint with a hook that moves at a constant rate until the dough ruptures. The load (resistance) in Brabender units on the vertical axis versus the extension length (cm) on the horizontal axis is the called the Extensogram (Figure 26.9). A greater height and area under the curve indicates greater flour strength. The overall shape of the curve, or the ratio of maximum resistance, R_{max} (maximum height of the curve) to extensibility, E, gives an estimation of the dough's viscoelastic balance. Low curves produce low R_{max}/E ratios and suggest a predominance of viscosity over elasticity.
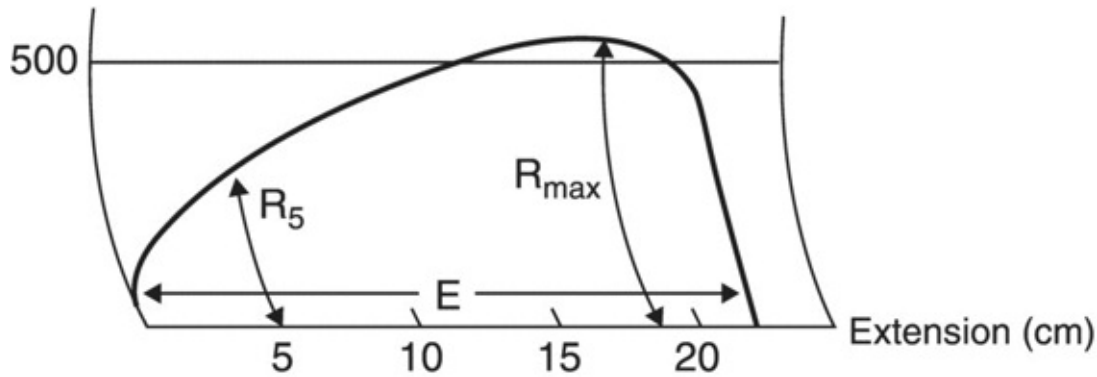
Figure 26.9 Extensogram showing extensibility (E), resistance at a constant extension of 5 cm (R_5) and maximum resistance (R_{max}).

In the Alveograph, a piece of dough is mounted between two collars, and a bubble is blown by introducing air at constant flow rate beneath the dough membrane. The pressure differential relative to atmospheric pressure is recorded as a dough bubble appears. The bubble thins out until a hole appears, and the pressure differential drops to zero. The curves and the characteristic shapes of the Alveogram (Figure 26.10) present a maximum pressure differential, P which is related to empirical dough properties such as stiffness, shortness or tightness. The parameter L is related to how much the dough will stretch under pressure before breaking, similar to extensibility. The third parameter W, is the area under the curve and represents the energy needed to deform the dough. Table 26.3 shows the general relationship of Alveograph parameters with flour quality and products.
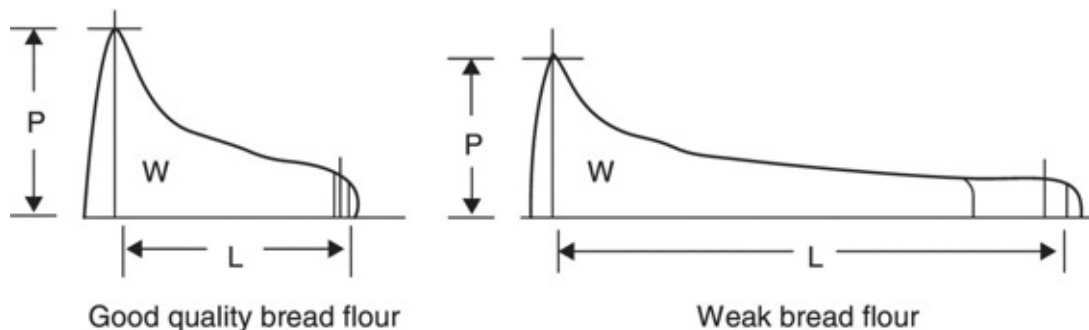
Figure 26.10 The Alveograph characteristic curves.

Table 26.3 The relationship of Alveograph parameters with flour quality and products

W	P (mm)	Flour quality	Type of products
~100	25–40	Weak	Wafers and ice-cream cone
	40–50		Cookies
~170	55	Medium	Salt biscuits
	62		Baguettes
>250	70	Strong	Croissants
	80		Buns

Despite having various means of measuring dough rheology, it is worth noting that most of the shear rates applied in dough rheology physical tests do not comply with the actual shear rates experienced during the bread making process. For example, a Farinograph measurement at a consistency of 500 BU is at shear rates of about 10 s^{-1} but the shear rates in a mechanical dough development mixer are in the range $10–100 \text{ s}^{-1}$ (Menjivar 1989). The extensional rates in both the Brabender Extensograph and the Chopin Alveograph are between 0.1 and 1 s^{-1} which are at least 100-fold higher than those in the real bread making process (Huang and Kokini 1999). The strains exerted by the DOSM are small and generally in the range of 0.1–5% while the strains experienced by bread dough can range from 100% during sheeting, 1000% during fermentation and oven-rise and up to 500 000% during mixing (Menjivar 1989). This mismatch is note worthy when interpreting these rheological data.

Bread dough rheology

Wheat flour dough is reported to exhibit various non-Newtonian behaviors including apparent yield stress, non-linear shear-thinning, and thixotropy (Weipert 1990). At low strains, viscosity is high and dough structure seems to be intact. In contrast, high strains lead to a large disorientation and destruction of dough structure, hence reduced viscosity (Bueche 1969; MacRitchie 1985). The strain hardening effect of dough arises when the stress increases more than proportionally to the increasing strain at a constant strain rate (van Vliet and others 1992; Dobraszczyk and Roberts 1994). It is a powerful tool for bulk rheological properties of dough that determines bread making performance very well. The elastic component in dough results in the increase in stress with increasing strain while the viscosity property results in the increase in stress with increasing strain rate (Janssen and others 1996). Large deformation tests such as the uniaxial and biaxial extension tests are used to determine the strain hardening index, n using the power law, $\sigma = K\varepsilon^n$ or the exponential equation, $\sigma = K\exp^{n\varepsilon}$, where σ is the stress and ε is the true strain (Dobraszczyk and Roberts 1994; van Vliet 2008). Rheological properties of dough are also markedly dependent on the deformation history having a relaxation time in the order of 100 s (Bloksma 1971). The relaxation time is the time required for the stress to decrease 36.8% (or $1/e$) of its value at the moment the deformation was stopped. In reviewing the rheological parameters measured over a wide range of bread dough samples, some rheological data collected from recent work on dough using fundamental and empirical methods are provided in Table 26.4 and Table 26.5, respectively.

Table 26.4 Range of dough rheological properties measured from fundamental test and characterization methods

Test type	Test method		Rheological properties			Research
	Shear viscometry	Shear rates (s⁻¹)	Consistency coefficient, K (Pa sⁿ)	Flow behavior index, n	Apparent viscosity (Pa s)	
		0.9644	–	–	1000–6000[a]	Uthayaku and others (1999)
		156	3.58–6.69	0.43–0.70	0.562–1.104	Sabanis and Tzia (2010
Rheometer	Oscillatory	Frequency sweep (Hz)	Storage modulus, G' (Pa)	Loss modulus, G'' (Pa)	Tan ϕ	
		0.005–100	6000–50000	1500–32 000	–	Correa and others (2c
		0.1	16 300–16 500	5200–54 000	0.319–0.327	Newberry others (2c
		0.1–10	6330–19 100	2460–7020	0.366–0.425	Angioloni others (2c
		0.1–10	11 000–42 800	–	0.27–0.40	Peressini Sensidoni (2009)
		0.1–10	9267–12 878	5004–6526	0.51–0.54	Balestra a others (2c
		0.1–100	22 4148–57 494	–	0.1–1.5	Upadhyay others (2c
		1–50	13 000–17 500	4290–5690	0.32–0.33	Lynch and others (2c
		Temperature sweep (°C)				
		25–100	20 000–300 000	10 000–90 000	0.11–0.45	Migliori a Gabriele (

[a]Maximum values.

Table 26.5 Range of dough rheological properties measured from empirical test and characterization methods

Test type	Rheological characterization			Researcher
Farinograph	Water absorption	Dough development	Dough stability	

	(g/100 g)	time (min)	(min)	
	74.6–77	5.5–7.0	2.5–6.5	Indrani and others (2010)
	61.10–67.30	1.10–3.60	1.60–6.10	Ibrahim and others (2010)
	60.8–71.1	7.2–13.2	4.5–17.1	Tong and others (2010)
	58.2–61.3	3.1–5.2	3.2–14.6	Gomez and others (2011a)
	50.7–59.9	7.1–12.4	11.0–20.9	Lopez-Guel and others (2012)
	61.2–73.7	1.7–7.5	2.5–14.7	Rieder and others (2012)
	58.2–65.9	3.0–6.7	10.6–15.9	Gomez and others (2011b)
	58.8–62.5	2.1–7.9	3.6–9.1	Mohammed and others (2012)
	61.4–63.8	1.4–2.4	7.1–11.5	Dagdelen and Gocmen (2007)
	55.0–56.7	19.0–21.8	20.3–23.2	Rosales-Juarez and others (2008)
	55.8–57.3	6.8–9.2	13.4–20.1	Pescador-Piedra and others (2009)
	53.6–57.0	1.53–2.53	1.40–13.07	Paraskevopoulou and others (2010)
	56.2–72.7	1.2–11.9	2.1–10.9	Gul and others (2009)
	50.3–62.3	1.8–11.0	1.5–10.5	Skendi and others (2010)
	56–73	1.0–5.0	1.5–6.5	Mohsen and others (2010)
Extensograph	**Resistance to extension (BU)**	**Extensibility (mm)**	**Area (cm²)**	
	280–360	101–140	60–85	Indrani and others (2011
	556–798	101–159	87–176	Tong and others (2010)
	310–560	84–170	53–138	Mohammed and others (2012)
	232.7–604.7	70.3–146.7	30.7–114	Gul and others (2009)

	385–689	81.68–112.31	57.1–81.1	Boz and others (2010)
	75–270	75–145	10–50	Mohsen and others (2010)
Mixograph	**Max. resistance to extension (g)**	**Extensibility (mm)**		
	19.19–55.18	16.83–31.41		Han and Koh (2011)
	Mixing time (min)	**Peak height (%)**		
	3.7–4.8	46–54		Asghar and others (2009)
Alveograph	P **(mmH$_2$O)**	L **(mmH$_2$O)**	W **(J×10^4)**	
	48–93	25–108	46–338	Gomez and others (2011a)
	68.00–99.46	124.60–145.68	281.88–388.53	Gomez and others (2008a)
	90–231	23–89	95–440	Pecivova and others (2010)
	66–80	97–130	242–300	Ktenioudaki and others (2010)
Amylograph	**Gelatinization temperature (C)**	**Peak viscosity (BU)**	**Hot paste viscosity (BU)**	
	71.0–73.6	306–571	233–378	Indrani and others (2011)

Cake batter rheology

The most common test conducted to measure cake batter rheology is the flow test using a viscometer where viscosities are measured as the spindle rotates in the batter at a specific rate. The apparent viscosities refer to a shear rate either in revolutions per minute (rpm) or per second. The rheometers are versatile for measuring rheological properties as they measure shear stress over a shear rate range enabling the behavior of fluid to be characterized by fitting into the shear stress–shear rate curve (Figure 26.3). The power law (Equation 26.5) is adopted where rheological properties of consistency coefficient and flow behavior index give an indication of flow characteristics. The cylindrical flow test geometrical configuration is used for the flow test while the plate–plate configuration is used to determine elastic and viscous components. The ranges of test methods used and the rheological properties obtained are listed in Table 26.6. The cake batter studies reported in Table 26.6 include a wide range of batter types from eggless to using whole eggs, egg albumin powder, and/or various functional ingredients at various degrees of aeration.

Table 26.6 Fundamental rheological test methods and properties performed on cake batter

Test type	Test method	Test range	Rheological properties			Researche
Flow test	Viscometer	Shear rates (rpm)	Consistency coefficient, K (Pas^n)	Flow behaviour index, n	Apparent viscosity (cP)	
		20[a]			18 600–30 000	Kumari and others (2011)
		20[a]			20 000–46 400	Ashwini and others (2009)
		20[a]			19 200–32 000	Rajiv and others (2011)
		20[a]			14 400–28 800	Sowmya and others (2009)
		1–50[a]	21.5–162.5	0.2528–0.5930		Akbulut and Bilgicli (2010)
		10–200	0.468–20.21	0.244–0.681		Lebesi and Tzia (2011)
		N/A[b]	12.98–17.38	0.423–0.511		Gujral and others (2003)
		N/A	1.23–38.36	0.58–0.81		Ronda and others (2011)
	Rheometer	Shear rates (s^{-1})	Consistency coefficient, K (Pas^n)	Flow behaviour index, n	Apparent viscosity (cP)	
		0.07–10	31.2–64.2	0.61–0.72		Meza and others (2011)
		0.1–10	19.99–338.11	0.25–0.42		Kalinga and Mishra (2009)
		0–50	31.93–481.19	0.33–0.51		Gomez and others (2010)

		0–50	21.7–78.82	0.3834–0.5808		Gomez and others (2008b)
		0.1–100	9–63	0.60–0.85		Chesterton and others (2011)
		0–200	5.00–26.36	0.68–0.88		Sakiyan and others (2004)
		0.05–200	17.7–52.0	0.31–0.54		Psimouli and Oreopoulou (2012)
		1–200	12.780–111.830	0.399–0.623		Turabi and others (2008)
		10–200	12.56–19.63	0.60–0.66		Tan and others (2011)
Oscillatory	**Rheometer**	**Frequency sweep (Hz)**	**Storage modulus, *G'* (Pa)**	**Loss modulus, *G"* (Pa)**	**Complex viscosity (Pa s)**	
		0.01–1	4–200	10–300		Meza and others (2011)
		0.1–10	41–193	46–173	68–243[c]	Gomez and others (2008b)
		0.1–10	2.39–91.43	7.94–117.48		Ronda and others (2011)
		0.1–20	0–6500	0–2600		Kalinga and Mishra (2009)
		0.1–10	59–1223	83–1037	13–165	Sahi and Alava (2003)
		Temperature sweep (ºC)	**Storage modulus, *G'* (Pa)**	**Loss modulus, *G"* (Pa)**		
		21–150	0.8–5000	–		Mleko and others (2010)

			25–170	10–40 000	10–5000		Kalinga and Mishra (2009)

[a] Spindle no. 7,

[b] spindle no. 18,

[c] at 1 Hz.

Conclusions

Rheological characterisation of dough is complex as it is significantly dependent on the stress, strain, rate, and history. At the moment, there are no standard methods for fundamental testing as compared to the empirical test methods where the AACC and ICC have approved. Despite the variance in values of rheological properties obtained through the differing approaches of fundamental measurements, they should be comparable universally, *i.e.* not affected by the measurement method or the sample dimensions as it is the characterisation of the material itself. In practice, the rheological measurements to be adopted shall depend on the purpose of the measurements and parameters needed. The choice of test range and speed should be related to the reason of testing. The extra challenge of bakery products research is the handling of yeasted dough samples and highly aerated cake batter foams.

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Part 5
Bread

27
Manufacture

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Introduction

Bread has been a staple food for many cultures across the world. It is one of the earliest "processed" foods made and consumed by humans. As shown by archeological discoveries, the first bread eaten by our human ancestors was most likely a quick bread, made by mixing flour with water and baking the dough on hot stones. Fermented bread was first made by the ancient Egyptians more than 5000 years ago (3000 BC). Specially designed bread-baking ovens were used as early as 2500 BC, where bread was baked on the inner surface of the ovens (Holloway 2012).

Bread is a "balanced" product, providing a good source of energy, protein, vitamins (particular the B group vitamins), minerals, and dietary fiber. With the rapid progress and development in agriculture and industrial technologies, white bread, which used to be a premium product for centuries, became more affordable and plentiful. New trends over the past two decades, however, have focused on healthy, traditional, and organic foods. Therefore bakeries using traditional ingredients and techniques, such as sourdough, wholemeal, and multigrain bread, have become more popular. Compared to white bread, brown, multigrain, and wholemeal bread contain more dietary fiber, minerals, and vitamins. However, white bread provides better bioavailability of some micronutrients such as iron. Nowadays, it is also a common practice for manufacturers to fortify or enrich some of the micronutrients in bread.

For celiac patients, gluten-free bread has been developed from varieties of flour such as rice, rye, soy sorghum, cassava, and so on. Due to the lack of a gluten network in such bread, some hydrocolloids (such as xanthan gum, guar gum, and hydroxypropylmethylcellulose) and proteins (such as soy protein isolate and whey proteins) have to be added to increase water absorption of dough, induce dough strengthening, and increase dough gas retention ability. With these substances, the texture and structure of the gluten-free bread is comparable to wheat-flour bread (Therdthai and others 2007).

Because bread is a carbohydrate-rich product containing a high amount of rapidly digestible starch, it probably has a high glycemic index (GI). So people may feel hungry shortly after having consumed bread, which could encourage them to eat more of it than the body requires, which is a concern from the viewpoint of obesity. There are many ways to decrease the GI of bread. In the presence of proteins in bread, the digestibility of starch may be reduced, depending on its interaction with the proteins. For example, glutenins could act as a barrier towards starch digestibility by gluing proteins into the matrix surrounding starch granules. Abundance of disulfide-bonded proteins is another factor that reduces starch digestibility. From *in vitro* starch digestibility analysis, the concentration of digested products from regular white bread was lower than that from gluten-free bread. In the wheat-flour bread system, starch is at the core surrounded by protein networks that may slow down its hydrolysis rate in the lumen of the small intestine (Wong and others 2009).

Recently, freshly baked bread became one of the most popular bread products. To be able to serve freshly baked bread in shops, baking time has to be reduced. Therefore, a bread making technology with partial baking, also referred as bake off technology (BOT), has been developed. The process is composed of two baking stages (Bárcenas, Rosell 2006). The first baking stage produces partially baked bread with aerated crumb but the brown crust is not developed. The bread obtained is frozen until the second baking stage. The second baking,

also referred to as full baking, evaporates water from the surface layers of bread to form a brown crust through the Maillard reaction and caramelization, and develops and releases flavor (Altamirano-Fortoul, Rosell 2011). This process allows freshly baked bread to be served in shops or at home as ordered within a very short time.

Bread can be broadly classified as leavened and unleavened. Leavened bread is made from dough containing leavening agents. The leavening agents include baker's yeast (usually *Saccharomyces cerevisiae*) and baking powders consisting of baking soda (sodium bicarbonate), acids, and inert fillers. Bread is leavened or aerated by carbon dioxide produced either by yeast fermentation or the baking powders. Unleavened bread is made without fermentation or gas producing agents, therefore the baked bread is often flat and dense, and hence it is sometimes called flat bread. Bread is also often classified as yeast bread and quick bread. For yeast bread, the dough requires proofing, which is a period of time at controlled temperature and humidity, prior to baking. This is to allow the yeast to ferment at its maximum rate. The fermentation increases the volume of dough considerably. Examples of yeast bread include the most common white bread, different styles of brown bread, wholegrain (or called wholemeal) bread, and many types of gourmet bread (mixed grain, fruit bread, and so on). Quick bread is made by mixing the ingredients and immediately baking the dough without proofing, therefore it is a much quicker process. Quick bread may or may not contain baking powders. When baking powders are absent, the bread may still be leavened by steam to some extent. Examples of quick bread include pancakes, crepes, tortillas, muffins, focaccia, and Arabic bread.

The rest of this chapter focuses on typical yeast bread, which is the largest category of bread produced by the bakery industry today. The production of yeast bread shares the same fundamentals with other types of bread and its process can be easily adopted or modified for the others.

Bread making process technology

Bread manufacture consists of a series of processes including mixing, fermentation, sheeting and molding, proofing, baking, cooling, and slicing (optional), as shown in Figure 27.1. Each of the processes plays a unique role in the development of dough/bread towards the final product quality; therefore, they all need to be carefully operated within a prescribed range.
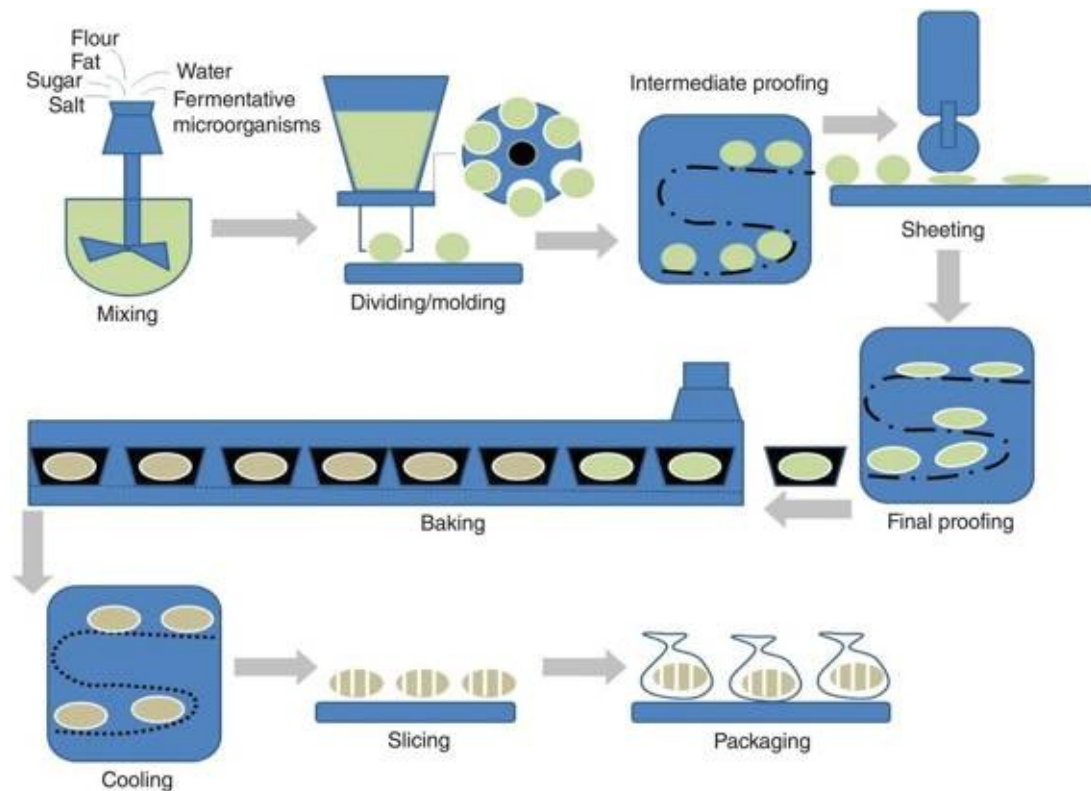
Figure 27.1 Process flow diagram of bread making.

Dough mixing

Mixing is one of the important steps in the bread making process to form dough through three major mechanisms: homogenization, gluten development, and aeration. It is a crucial process that controls the pore structure of the bread. When the ingredients are mixed with water, hydration occurs at the surface of the flour particles due to mechanical energy input from progressive mixing. Locally connected structures are consequently transformed to a gluten network. The development of the gluten network depends on types of deformation such as shear and elongation. Conventional mixers usually provide combined deformation flows. The gluten network could become stronger by increasing mixing energy from 20 to 60 kJ/kg (Shehzad and others 2010). Peighambardoust and others (2010) compared a steady shear-only mixing process with a mixing process of combined steady shear and extensional forces (z-blade mixing). At low moisture content (around 50%), both mixing processes yielded similar static dough density measured immediately after mixing. This was because the low moisture content dough had high consistency and tended to physically trap air bubbles well upon mixing. Therefore the effect of deformation flows on aeration was not clear. In addition, shearing dough at a low rotation speed (1 rpm) yielded similar mechanical aeration during mixing and dough volume after proofing. An increase in the rotation speed could break down the gluten network, however, and thereby decrease its gas retaining ability

during proofing and baking.

Aeration performance can be evaluated from measuring dough density. Static dough density indicates air occlusion during mixing. Dynamic dough density is usually monitored to estimate the amount of the gas retained during proofing. However, it might underestimate the production of carbon dioxide gas by yeast due to the loss into the atmosphere (Chiotellis, Campbell 2003). By scaling up the mixer or increasing the Reynolds number, the degree of steady state aeration and turnover rate were increased. In the industrial scale Chorleywood Bread Process (CBP), excessive aeration was claimed as a major problem. To rectify this problem, pressure-vacuum mixing at 2.5–0.35 bar was used. An increase in pressure above atmospheric pressure during the early stage of mixing can increase oxygen and enhance dough development. This is because oxygen is required for an oxidizing improver, ascorbic acid, so that it performs its effect on dough improvement. Oxygen is absorbed from air through the outer surface of dough and from the entrained gas through the dough–bubble interface (Martin and others 2004b). Martin and others (2004a) reported that an increase in the mixer headspace pressure increased bubble number density in the dough and mean bubble size. At the last stage of mixing, pressure should be reduced below atmospheric pressure to develop a finer bread crumb. Chin and others (2004) studied the effect of direction and size of a pressure step-change during mixing on gas turnover. By using a pressure step-decrease, gas volume reached its steady state quickly and the rate of gas turnover was over twice as large. The turnover times were less than 30 s. By increasing the size of pressure step-increase, the gas turnover time was reduced. The rate of gas turnover could be increased when weak flour was used, however, regardless of the direction and size of a pressure step-change during mixing.

Dough fermentation and proofing

After the mixing process, a three-dimensional protein network is formed resulting in a viscoelastic material. During proofing, yeast (baker's yeast is usually *Saccharomyces cerevisiae*) is the key microbial component for fermentation. During fermentation, the viscoelastic material expands due to the production of carbon dioxide gas by yeast metabolism, which transforms carbohydrates into carbon dioxide and ethyl alcohol. For the first 100 min, hexoses are fermented and when these are depleted, maltose is fermented. The carbon dioxide gas is dissolved in the aqueous phase of dough; it then migrates to form initial nuclei of air bubbles during sheeting, resulting in bubble growth and coalescence in the pseudoplastic foam. The ethyl alcohol affects the colloidal nature of wheat proteins and alters the interfacial tension within the dough. Therefore, yeast activity during fermentation has two functions: modification of dough matrix elasticity, and expanding gas cells (Elmehdi and others 2003). This leads to the development of bread volume and crumb structure, depending on the generation and retention of gases. The production of gases is dependent on yeast activity, while the retention of gases is related to bubble characteristics. The results of a study using X-ray tomography also confirmed that gas production was mainly responsible for dough expansion kinetics; however, the stability of dough volume was dependent on dough rheological properties (Shehzad and others 2010). Primo-Martin and others (2010) reported that a short proofing time should give finer crumb morphology, closer structure, and smaller gas cells with less gas cell interconnection. An increase in fermentation time can increase proteolysis and thereby increase the amount of free amino acids which are precursors of

Strecker aldehydes. The 'malty' aroma compounds are enhanced (Zehentbauer, Grosch 1998). Generally, fermentation can be divided into three stages including a lag stage, a positive acceleration stage, and a negative acceleration stage. Dough volume could be simulated using a modified Gompertz model (Romano and others 2007).

At the beginning of proofing, the concentration of carbon dioxide gas in the liquid phase is low. As a result, the driving force for transferring carbon dioxide gas into the bubbles is still weak. As the fermentation progresses, the concentration of carbon dioxide increases and eventually the carbon dioxide can inflate the bubbles. An increase in proofing temperature enhances the accumulation of carbon dioxide gas in the liquid phase, due to an increase of yeast activity (Chiotellis, Campbell 2003). Moreover, the solubility of gas is decreased at a high temperature. Gabric and others (2011) reported that the solubility of carbon dioxide was reduced from 1.6×10^{-5} to 0.5×10^{-5} g CO_2 kPa^{-1} g^{-1} when the temperature was increased from 0 to 50 °C. Therefore, the inflation rate of gas into the bubbles was improved. However, a low fermentation temperature slows down the oxidative degradation of linoleic acid; as a result, the amount of off-odor compounds including 1-octen-3-one and 2-nonenal might be reduced (Zehentbauer and Grosch 1998). In addition to increasing fermentation temperature, the rate of mass transfer of carbon dioxide gas into the bubbles can also be improved by an increase in head space pressure during mixing. The increased pressure during mixing also increases the number of bubbles. An increase in the number of bubbles and a decrease in their mean diameter can speed up the mass transfer for the gas into the bubbles, due to a high interfacial area for mass transfer. Bubbles are expanded to the maximum level and then coalesce (Chiotellis, Campbell 2003).

Lactic acid fermentation is also popular in bread making, producing so-called "sourdough bread". Dough is fermented by lactic acid bacteria for several hours to develop a unique flavor. Dominant lactic acid bacteria in sourdoughs are varied depending on flour type and country, for example, *Lactobacillus plantarum, Lactobacillus curvatus, Lactobacillus paracasei, Lactobacillus sanfranciscensis, Lactobacillus pentosus, Lactobacillus paraplantarum, Lactobacillus sakei, Lactobacillus brevis, Pediococcus pentosaceus, Leuconostoc mesenteroides, Leuconostoc citreum, Weissella cibaria, Weissella confusa, Lactococcus lactis*, and *Enterococcus hurae* (Robert and others 2009). The outcome of homofermentation is mainly lactic acid through glycolysis, starting from glucose. The homofermentative lactic acid bacteria are good at acidification. In heterofermentation, a mixture of lactic acid and acetic acid is produced. The heterofermentative lactic acid bacteria are also known as "aromatic microflora". Moreover, acetic acid has an antifungal activity which helps extend the shelf-life of fermented bread. Sourdough fermentation can be performed in either firm dough or a liquid suspension of flour in water. During fermentation, the temperature should be controlled to ensure dough yield, acidification rate, and flavor development. Generally, sourdough is classified into three types: type I, type II and type III. Type I is a traditional sourdough style which is restarted using a part of the previously fermented dough. Type II is usually used in industrial bakeries. The fermentation is started from the adapted bacteria possibly in liquid form. Type III is in dried form and is usually used in industrial bakeries because there is less variation of fermentation performance. Drying technology should be carefully selected to ensure the activity of sourdough. Normally drum drying and spray drying can be used (Decock and Cappelle 2005).

Dough sheeting and molding

Dough sheeting is the process of passing the dough through counter-rotating rollers. The ratio of feeding thickness to roller gap width plays an important role in yielding strains and stresses in the dough. In contrast, the speed of the rollers is less important. During sheeting, large gas bubbles within the dough can be subdivided to improve the bubble distribution in the dough and thereby yield a fine structure of bread crumb. Normally, sheeting tends to increase the amount of elongated bubbles due to gluten alignment (Engmann and others 2005). By passing through the sheeting rollers many times, dough structure could be similar to that observed in dough mixed in a conventional mixer. However, the amount of energy required for sheeting is only 10—15% of that required for mixing (Qi and others 2008). Repeated sheeting can either build up or break down a protein network structure. Increasing the number of repeated sheeting also reduces dough resistance and increases dough extendibility. Therefore, sheeting is a process that significantly contributes to the development of dough and bread structure. After sheeting, dough is molded to form an appropriate shape for the next processing step. Rolling sheets in the same direction as the preparative rolling showed around 10% spread. However, those sheets turned by 90° showed no spread and some even shrank. Therefore the direction of sheeting affected elongational stresses. To reduce the dough stress, folding back across the width of a sheet should be applied (Engmann and others 2005). In industrial sheeting lines, multiple sheeting rolls were managed to firstly stretch dough in one direction and then cross-wise in the other direction (Chakrabarti-Bell and others 2010).

The major problem found in sheeting and molding is the dough surface sticking to the sheeting rollers during sheeting and dough spring-back after sheeting. The degree of sticking depends on dough rheology, which is related to water content, starch content, wheat genetics, mixing procedure, and temperature (Tanner and others 2008). Viscosity of dough has been used to estimate the thickness of sheeted dough, roller force, torque, and work input (Qi and others 2008). In addition to stickiness, another usual problem is variation of dough sheet thickness due to the elasticity of dough and the difficulty of controlling mass flow rate during the sheeting. As a result, cutting the dough pieces may not be well controlled. When dough is overdeveloped during mixing and then becomes extensible, the control of mass flow rate improves (Chakrabarti-Bell and others 2010). So far, various studies have predicted dough thickness using mathematical models, for example, the empirical model (Engmann and others 2005), van der Waals model (Xiao and others 2007), linear viscoelastic, constitutive model (Qi and others 2008), two-dimensional finite-element simulation based on rolling geometry and rheological data with slip (Mitsoulis and Hatzikiriakos 2009), and the modified Bergstrom—Boyce model (Chakrabarti-Bell and others 2010).

Baking

Baking is the step which transforms dough into bread, including crust and crumb, under the impact of heat. The rate and amount of heat applied during baking are key parameters affecting the final quality of the bread. To obtain the desired bread quality, the impact of baking parameters (heat source, airflow pattern, flow rate, oven load, baking time) and their interactions should be understood. Based on the relationship between baking parameters and bread quality, baking conditions could be optimized in accordance with the desired bread

characteristics (Therdthai and Zhou 2003). At the beginning of baking when heat starts to be transferred to dough, yeast fermentation is still active resulting in an increased amount of carbon dioxide gas. When the temperature is too high (about 55 °C), yeast is inactivated; only an expansion of gas is observed without any new production of carbon dioxide gas, leading to so-called "oven-spring". The oven-spring occurs until dough plasticity is decreased and cells in the dough are interconnected due to starch gelatinization and protein coagulation (at around 60–90 °C). Then the carbon dioxide gas is vaporized, while ethanol is soluble in the liquid phase of dough. When temperature reaches 100 °C, moisture is vaporized. There is around 10–20% baking loss which is related to moisture loss.

During the oven-spring, good extensibility of the dough surface is required to prevent the crust tearing. Applying steam to the dough surface can help maintain its extensibility for a certain period. Oven-spring can thus take place for a longer during baking, so that crust formation does not occur too early and bread volume will not be too small. The amount of carbon dioxide is also increased, due to a late inactivation of yeast activity. In addition to deferring crust formation, steaming during baking has a significant impact on crust color, glossiness, and mechanical properties due to surface starch gelatinization and the protein–starch network. An increase in steam supply significantly decreases crust color and crumb firmness, but increases glossiness. In addition, the vapor transfer rate and crust permeability are decreased (Altamirano-Fortoul and others 2012). Heat penetration into crumb is enhanced. However, Le-bail and others (2011) found that the heating rate of baking with a low amount of steam was significantly higher than that of baking with a high amount of steam. This was because excess steam caused condensation, resulting in a negative effect on the heating rate. When steaming was too low, crust tearing and a thick crust were observed. In addition, the vapor permeability of the crust might also be too low, which makes it difficult to maintain crispness during storage. Therefore, Altamirano-Fortoul and others (2012) recommended a low-medium amount of steam to obtain a thin crust that ensures reasonable permeability of moisture during storage. As a result, the bread crust should remain brittle for longer after baking. In batch baking ovens, steaming is applied during the initial baking stage where humidity is controlled by opening a chimney. In continuous baking ovens, the temperature and humidity are normally controlled individually in each zone (Le-bail and others 2011).

Recently, crustless bread was launched on to the market in the United States, Italy, and Spain. This is mainly acrylamide, which is a probable human carcinogen, has been found in bread crust (Ahrné and others 2007). In addition, in the United States, some bread for children is crustless due to consumer-oriented product design. However, almost all crustless bread is made by cutting the crust off the regular bread. The remaining bread crumb was about 55% of the actual loaf. Mondal and Datta (2010) described a new technology for making crustless bread. To prevent crust formation during baking, evaporation at the dough surface had to be slowed down by spraying water (2 ml per 8.6 min interval) on the dough surface intermittently at a controlled temperature (168 °C). Therefore the dough surface temperature was not high enough to enhance evaporation. However, the water spraying could change the thermophysical properties of dough and the pattern of heat and mass transfer during baking.

In crumb formation, dough is transformed to a rigid structure through protein coagulation and starch gelatinization. During the mixing process, the intramolecular and intermolecular disulfide bonds of proteins are used to form a gluten matrix that enables the dough to trap

air. During baking, when the temperature reaches 70 °C, the structure of proteins – particularly gliadins – is changed, resulting in crumb formation. Singh (2005) reported that the amount of extractable proteins (the proteins left after sonication at 15 W for 45 s) was decreased as baking time was increased. The maximum decrease in the extractable proteins was observed at the loaf centre (loaf centre temperature was at 60 °C and 90 °C after 5 and 20 min baking time, respectively), not at the surface. This was probably due to the variation of temperature and moisture content within the loaf. The increased amount of unextractable proteins or the insolubility of proteins related to the formation of cross-linking disulfide bonds during baking. The cross-linking disulfide bonds mainly caused the aggregation and polymerization of proteins during baking. The high molecular weight of the polymers in the insoluble proteins was confirmed by them being unbreakable by the sonification. During mixing, gluten proteins are hydrated and form a three-dimensional structure dispersed in starch granules. With dough is heated during baking, the starch granules are prone to swelling and then gelatinization. The gelatinization temperature of wheat flour is around 51–79 °C. Ingredients in a dough formula may affect the gelatinization–gelation process or pasting properties. For example, the addition of sugar tends to increase starch gelatinization temperature and pasting viscosity due to a reduction of available water. The addition of salt increases pasting consistency due to the improved integrity of starch granules (Le-bail and others 2011).

A baking oven can be powered by electricity or fuel/gas. Small-scale batch baking ovens are normally electrically powered. For a large-scale industrial production, continuous ovens are used and often powered by fuel/gas. The major components of a baking oven include baking chamber, heating system, and burners. The baking chamber is designed as a rectangular box formed by steel lining sheets supported by a steel frame. The top, sides, and bottom of the oven walls may be insulated with 2-inch rock wool. An oven's heating energy can be supplied by fuel oil, natural gas, propane-butane, and electricity. Generally, 1 kg bread requires around 340–450 BTU to complete baking. However, additional energy is required to heat the tins (around 90 BTU/kg of dough) and to compensate for losses through the walls. In a direct heating system, burners are installed below or above the trays in the oven cavity. They are arranged to form control zones. Each zone has an independent air supply, a modulating temperature controller, and a burner to manipulate the temperature in the zone. In contrast, in an indirect heating system, burners are installed outside the oven cavity. The system requires burners, combustion tunnels, radiator tubes, ducts, recirculating fans, exhausts with dampers, and control and safety devices. In the oven chamber, the heating system is operated at a negative pressure of approximately 12 mm water gauge to prevent the products from being contaminated by the gas if any leakage occurs in the duct. In an indirect gas-fired burner system, 20% of additional energy is normally required due to the loss to an enclosed system (Matz 1989).

To improve the conventional baking ovens described earlier, impingement ovens, another type of forced convection oven has been studied. In an impingement oven, forced convective heat transfer is imparted on product surface, using a very high air velocity. Wahlby and others (2000) compared the heating rate and the consequent bread development for buns baked inside a conventional forced convection oven and an impingement oven. Bread baked in the impingement oven tended to have an increased heating rate at the crumb centre and crust surface. However, at the crumb centre, the trend was not statistically different from that baked inside the conventional forced convection oven. Due to the higher heating rate on the

surface, the crust of bread baked inside the impingement oven was developed earlier and was eventually darker. The early development of crust also caused an increased weight loss and possibly a thicker crust. However, it did not significantly affect the shape and volume of bread. Industrial impingement ovens are already used to bake high-moisture bakery products such as cakes, pizzas, and pies.

Microwave ovens have also been introduced into baking, due to their advantages in time saving and the improved nutritional quality of products (Decareau and Peterson 1986). However, microwave-baked products have not been fully accepted by consumers. This is mainly due to the difference in heat transfer modes between a conventional baking oven and a microwave oven. The microwave increases the product temperature rapidly by enhancing the movement of water molecules. Therefore the ambient temperature in the microwave oven is low. As a result, Maillard reactions at the dough surface may not be completed at the end of baking. In addition, a short baking time may cause incomplete starch gelatinization and flavor development (Sumnu, 2001). Verboven and others (2003) tried to modify a traditional microwave oven by combining it with natural and forced convection regimes. According to a computational fluid dynamics simulation, it was found that the mass transfer coefficient and the uniformity of heat transfer coefficient at the food surface could be significantly increased when air inlets and outlets were placed optimally, as well as when different types of fan were used. Keskin and others (2004) studied the baking performance inside a halogen lamp–microwave combination oven and compared it to a microwave oven and a conventional oven. The results showed an increased weight loss as more power from the microwave and the halogen lamp was applied. Because the halogen lamp provided only near-infrared radiation, its penetration depth was very limited. Crust was therefore formed earlier for baking under the halogen lamp. This caused a smaller volume and a higher weight loss. However, halogen lamp radiation enhanced the crust colour development which the microwave did not do properly.

These technologies have advantages and disadvantages against each other. The best outcome is achieved bycombining their advantages and applying each of them at the right time. Ideally, the microwave should be used to reduce the baking time, the conventional technique to reduce the condensation on the surface and lateral layer, and the halogen lamp to enhance the crust color development. It should be possible to use an optimized combination profile of these baking technologies to produce the best bread within the shortest time.

To improve oven efficiency, the effect of airflow patterns in a domestic forced convection oven on heat distribution was established by Noel and others (1998). The oven configuration was subsequently modified to obtain a more uniform heat distribution. Compared with a top-bottom radiant heat oven, a forced convection oven provided a larger heat flux for the same setting temperature. Therefore the setting temperature in a forced convection oven can be reduced to obtain the same quality bread as in a top-bottom radiant heat oven (Wahlby and others, 2000). An oven can be operated to provide an optimum heat flux from combined heat transfer modes to the top, bottom, and sides of a product (Carvalho and Nogueira 1997). Similarly, an oven can also be manipulated to achieve an optimum surface temperature profile (Therdthai and others 2002, 2004). A combined radiant and convection oven with direct recirculation and an optimum humidity control could be both cost effective and capable of producing bread with a more traditional home-baked appearance, which is one of the current market trends for bread.

Cooling

After baking, bread is normally cooled down, in order to be sliced or packaged. During cooling, crust temperature tends to decrease asymptotically towards cooling air temperature. Initially the crust temperature is higher than the temperature at loaf centre. Later, the opposite can be observed. Cooling time for a bread loaf is defined as the time needed to cool the loaf down from when it leaves the oven until its geometrical centre reaches 25 °C. A number of phenomena happen during this process. At the beginning of cooling, there is a high vapor pressure gradient between the crumb centre and the crust. Thus, heat and mass transfer is governed by evaporation– condensation inside the bread as well as radiant heat transfer at the curst surface. Later, the evaporation–condensation mechanism becomes less important, and radiation is also decreased. As a result, the cooling rate during the later stage of cooling is significantly decreased (Grenier and others 2002).

Cooling rate in the crust layer is higher than that in the crumb, due to water migration. Water migration is mainly observed in the crust layer, not the crumb as there is very little water diffusion within the crumb (Grenier and others 2002). Therefore, moisture loss during cooling is mainly from the crust layer and can be controlled by manipulating air temperature and relative humidity (Bailey and Cauvain 1993). Cooling rate can be rapid when the crust temperature is lower than the saturated vapor temperature in the bread crumb. However, condensation may occur below the crust when moisture from the crumb is transferred towards the crust with minimal evaporation. In contrast, the condensation below the crust is minimized when the crust temperature is higher than the saturated vapor temperature in the crumb; moreover, the moisture loss during cooling can be reduced. This is consistent with the slow cooling rate of crust temperature. At a high cooling air temperature, the partial water vapor pressure difference between the surrounding air and the crust is low, compared with cooling at a very low temperature. Therefore, control of evaporation during cooling is necessary to prevent accumulated moisture and thereby microbial growth (Grenier and others 2002).

As bread crumb is cooled down, retrogradation of amylose and amylopectin occurs. The retrogradation of amylose occurs within the first hour of cooling, whereas, the retrogradation of amylopectin occurs in the following few hours. The retrogradation of both amylose and amylopectin plays a key role in bread staling; however, the retrogradation of amylopectin seems to be a major contributor to crumb staling. The value of bread discarded due to staling can be quite high. To delay retrogradation, some of the ingredients (such as shortening and emulsifiers), cooling conditions, and storage conditions should be optimized (Ribotta and Le Bail 2007).

Moisture distribution plays an important role at the bread surface, where crust flaking and loss of crispness are major problems found during bread cooling. Crispness is generated when the starch and protein matrix is in the glassy state, which is related to water activity and moisture content (Stokes and Donald 2000). In fresh bread (within 24 h after baking), the moisture content of crust should be within 4.84–11.50 g/100 g. Altamirano-Fortoul and Rosell (2011) reported that a loss of crust mechanical properties was observed during the first 4 h of cooling, depending on bread type. The loss occurred at either a water activity ranging from 0.50–0.74 or a moisture content ranging from 9 to 15 /100 g. The increase in the moisture content of the crust was due to moisture migration from the crumb to the crust.

Although retrogradation is claimed as a key to bread crumb staling, it is not responsible for the loss of crust crispness. Primo-Martin and others (2007) used X-ray and differential scanning calorimetry to verify that starch retrogradation in the crust occurred only after 2 days of storage.

Slicing

Slicing is another important step in bread making to separate the non-brittle materials and create nearly-identical pieces with a defined geometry. Cutting by simply forcing a knife perpendicularly through a soft material is difficult. It can be achieved simply using slicing motion. A slicing device should be regularly honed or sharpened depending on cutting edge retention. Slicing performance is a function of some intrinsic properties of a blade, inclination, geometry, curvature, and the sharpened edge of the blade (Marsot and others 2007). In homogenous bread, all parameters can be easily optimized to obtain the best slicing performance. Bread containing layers or particles varying in stiffness and elasticity usually has a large variation in mechanical properties. Conventional slicing devices might not be the best solution. Recently, slicing devices excited electro-mechanically by ultrasound have been developed as an alternative option. Frequency is within 20–40 kHz. The slicing performance depends on blade geometry, direction of vibration relative to cutting direction, ultrasound frequency, and amplitude. The ultrasonic excitation significantly reduces cutting force, with the degree of reduction depending on the product type. An increase in cutting velocity causes an increased cutting force and cutting work (Arnold and others 2011). After an ultrasonic device was used, the cutting work and friction work of malted bread could be decreased from 0.804 and 0.107 J to 0.367 and 0.084 J, respectively (Schneider and others 2009).

Process monitoring and control

Online process monitoring and control of bread manufacturing is challenging, partly because many of the mechanisms in bread making are still not fully understood or quantitatively described, as pointed out earlier in this chapter. To make product quality consistent not only to satisfy regulatory requirements but also to obtain a maximum economic return for a company, however, demands a high degree of automation in bread production plants.

Currently, sequential control is well utilized in bread production lines to control different stages of the manufacturing process (mixing, molding, rounding, proofing, baking, and so on) and to coordinate between them. The main information used in such a system is the time or the duration of an operation, for example mixing time, proofing time, and baking time. Online monitoring systems with industrial computers, touch screens, programmable logic controllers (PLC), and supervisory control and data acquisition (SCADA) systems have been installed to fulfill the control objectives. However, such a control system is largely based on single-input single-output (SISO) processes, and the key concept is a simple on−off control without real-time feedback (Trystram 1997).

Besides the sequential control described earlier, feedback control systems have been implemented for mixing, dividing, proofing, baking, and cooling. For mixing, the temperature of the dough is measured and fed back to the control system until a predetermined final dough temperature (the set point) is achieved. As described earlier in this chapter, this is in an attempt to control the energy input to the dough, which is critical to the development of a gluten network in dough and therefore to the rheological properties of the dough. For dividing, the weight of a divided dough piece is measured and fed back to the control system, and underweight pieces are subsequently rejected. The nature of the controllers for these two processes is again simply an on−off control.

For proofing, the temperature and humidity of the prover are measured and controlled through a feedback system by continuously adjusting the steam supply. For baking, the temperature of the oven chamber is controlled by a feedback system through the manipulation of the electrical power input to the heating elements or of the rates of gas supply to the burners. The set point is a predetermined value according to the type of product and production rate. The controller is either a multilevel on−off controller or a proportional-integral-derivative (PID) controller.

The limited application of feedback control and the absence of advanced control (for example, robust non-linear control) in bread manufacturing are mainly due to the lack of high-quality online sensors and high-quality models of the processes. High-quality online sensors are desirable for the key process and product parameters, ranging from temperature, pressure, flow rate, and weight, to dough properties, moisture content, color, volume, and so on. Measurements from these sensors provide not only vital information on the current status of the process and products, but also the necessary feedback signals for a closed-loop system.

Unfortunately, there is a general lack of quality online sensors, particularly sensors for product quality attributes (dough properties, colour, shape, volume, and so on) for all food processes including bread baking. This lack of online sensors presents a major limitation to the development of high-level and high-performance automation systems (Trystram 1997).

For example, if an online sensor for dough structure was available, the mixing process could be controlled via a feedback control system directly based on the signal from this sensor, rather than based on the temperature of dough, as it is now. Some recently developed techniques such as image analysis, ultrasonic, and NIR (near-infrared) technologies might be able to provide reliable online sensors for baking products in the future. However, their wide applications in the bakery industry are yet to be seen.

Successfully designing an advanced process control system heavily depends on a good understanding of the process, its responses to the operation conditions, and their interactions. This understanding needs to be quantitative. In other words, a good model, particularly a good dynamic model, of the process needs to be established. Bread making involves complicated transformations from raw ingredients to dough and further to bread. This makes it very hard to establish a high-quality model. However, there have been persistent efforts and progress towards modeling the various stages of bread making using advanced modeling techniques.

For example, Therdthai and others (2002) showed that for a continuous industrial baking process the final quality attributes of bread, including crust colour, weight loss, and crumb temperature, were highly dependent on the surface temperature profile the bread experienced while traveling through the oven. Through mathematical modeling, an optimal surface temperature profile can be found. This clearly shows that a baking oven controlled at a constant temperature may not be adequate to produce a good product. Rather, the oven should be operated in such a way that produces the optimal surface temperature profile for the traveling bread, which depends on oven air temperature distribution and air velocity distribution. However, establishing a mathematical model to describe the relationship between oven operating parameters (such as gas supply rate and production load) and the heat and air distribution inside the whole oven is a prohibiting task. It has been shown that the computational fluid dynamics (CFD) modeling technique can be very useful in providing dynamic models for this complicated system (Therdthai and others 2003, 2004). Wong and others (2007) incorporated a feedback control system into a CFD model through user-defined functions to establish a new process control system with multiple decoupled PI controllers (Figure 27.2).
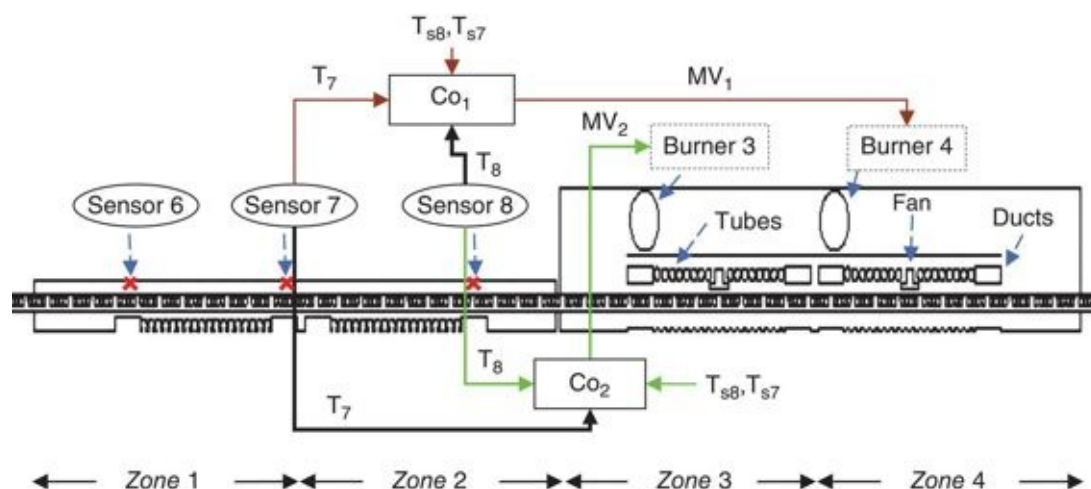
Figure 27.2 Control system in a continuous traveling-tray oven by computational fluid dynamics. (Wong, Zhou & Hua 2007. Reproduced with permission of Elsevier).

Conclusion

Bread has been and will continue to be a major food item for many people across the world. Bread manufacture consists of a series of processes including mixing, fermentation, sheeting and molding, proofing, baking, cooling, and perhaps also slicing. Each of the processes plays a unique role in the development of dough/bread towards the final product quality; therefore, they all need to be carefully maintained within a prescribed range. While new varieties of bread are developed according to the market trends, advanced process control and automation systems should also be designed and implemented for bread manufacturing, which requires more studies on the development of high-quality online sensors and process models for the various processes.

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Quality Control

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Introduction

If a number of different consumers were asked what qualities they looked for in a loaf of bread they would all have different views. It is soon recognized that bread quality is very much an individual perception. The subject of quality in bread is therefore a contentious issue. Quality means different things to different people, and no two people share the same opinion about a particular type of bread. However, cereal scientists and technologists are able to identify certain characteristics of each style of bread and determine the attributes that add to its quality and those that detract from it. In this chapter the issue of bread quality is tackled from the European perspective, and the factors that are considered to be important in the range of bread types that are popularly consumed in the United Kingdom and the rest of Europe are examined.

Appearance is the first visual assessment of a loaf, and key factors include the volume (size) of the bread as well as the color, particularly that of the crust and the shape of the loaf. The consumer is also likely to give the loaf a squeeze to obtain an idea of the softness so that a quick judgment can be made of the freshness. Crust color and softness are probably the two key issues consumers use to make their choice at the point of sale. There are various faults in the external appearance of loaves that can be readily identified as unacceptable. In this chapter, the more commonly encountered faults are described and, where possible, illustrated, and information is provided for remediating such faults when they occur.

Important quality issues arise from the style of bread under consideration. For example, a key factor for sandwich-type bread would be the uniform distribution of small-sized bubbles, which give the bread crumb its characteristic appearance and the physical strength to allow butter to be spread over the surface. For French baguettes, it is the crisp, flavorful crust that contributes most to eating quality, paired with the crumb being open and irregular in appearance. For these two bread types the production methods are essentially the same; the process must create the appropriate number and sizes of gas bubbles in the dough and ensure that they survive during subsequent processing. The process of creating and controlling bubble structure therefore makes a fundamental contribution to bread quality, and this chapter deals with the key mechanisms of structure control available to the baker as well the choice of ingredients, formulations, equipment, and processing methods that affect final product quality.

Bread quality changes with time. This is true for all types of bread, and storage generally leads to loss in quality. There are various factors that combine to make the bread go stale and eventually become unfit to be sold. The roles of ingredients and methods of mixing have a large impact on the shelf-life of bread. Staling is one of the main processes that causes bread to lose quality. Staling is a complex process and is related to changes in the starch. It is also referred to as chemical staling. Key factors involved in bread staling are examined in this chapter, and methods are outlined to explain how the processes leading to deterioration in quality can be slowed down to prolong the perceived freshness of bread.

Role of dough processing and bread quality

The style of bread dictates how the mixing, processing (molding), and baking are carried out. One would not want to produce French baguettes with a close crumb structure, and of course one would not want to produce an 800 g four-piece loaf with an open crumb structure like a baguette.

Whether making a four-piece or single-piece bread, the aim is to achieve the desired shape without causing damage to the bubbles that have been carefully developed during the mixing stage. Ninety percent of the final bread quality is achieved during mixing, so it is important to make sure processing continues to improve quality and avoids unnecessary damage. After mixing, the dough goes through several processing stages that change the shape of the dough and reorient the bubbles.

After dividing, the dough piece generally passes through a "rounding" stage, sometimes called first mold, and this stage uses equipment such as a conical molder to achieve a spherical dough piece ready to be passed through the final molder. After an initial resting period (intermediate proof), the dough piece moves to the final molder, which can be broken down into four sections (a sheeting stage, curling chain, pressure board, and guide bars), all of which influence the shape and length of the dough piece coming out of the end of the final molder.

Faults in loaf crumb structure, such as discolored coarse patches, streaks, and variations in softness are not uncommon in modern bread making. Many combinations of raw materials and dough processing stages can influence the occurrence of such faults, but they have a common origin. They are the direct result of instability in the structure formed during mixing and/or subsequent damage to the bubble structure during molding.

Dough mixing systems

Bulk ferment systems

Bulk fermentation doughs account for only around 1% of the bread produced in the United Kingdom, but they are still widely used in other European countries. The main reason the process is not used widely in the United Kingdom is the time required to develop the dough and the open crumb structure associated with bulk-fermented products. Before the dough can be divided the following steps must occur:

- All the ingredients must be mixed to a homogeneous mass that can take up to 30 min in a low speed mixer.
- The dough must be given a bulk resting period that can be 1–16 h or longer. The bulk resting time will be dependent on the flour strength, dough temperature, and yeast level and, of course, the bread characteristics required. At this stage the bakery would also need a temperature-controlled room with sufficient floor space to store the dough.
- Halfway through the bulk fermentation, the dough is given a "knock-back," a remixing to control bubble formation and help ensure that the dough does not form a skin on the surface.

- After completing the bulk fermentation period the dough can then be processed in a manner similar to that used for no-time doughs.

No-time dough systems

In a no-time dough system all the development is achieved in the mixer; after mixing is completed the dough is processed immediately, which would entail scaling, first molding, intermediate proof, final molding, final proof, and baking; from beginning to end the process can take approximately 2 h. Plant bakeries are the main users of no-time doughs (doughs in which all the development takes place in the mixing chamber), usually by means of the Chorleywood Bread Process (CBP) (Chamberlain and others 1962; Axford and others 1963; Chamberlain and Collins 1979).

In no-time doughs, the mixing process is critical to achieve optimum dough development and bubble structure. Typical examples of mixing equipment used to produce no-time doughs are shown in Figure 28.1.

(a)

Figure 28.1 Mixers used for no-time dough production. Pressure-vacuum, left; spiral, right. Courtesy of Campden BRI.

When using a high-speed mixer, a watt-hour meter, not a timer, should be used to control the mixing. Variations in dough batch size and consistency affect the time required to achieve a given energy input. For example, a soft dough will achieve the correct energy input at a lower rate than a tight dough will, so working to time will cause real problems with consistency in dough development.

Intense mechanical work during mixing is an essential part of the rapid dough development and one means by which the bulk fermentation stage is eliminated. As the mixing blade moves through the dough, air bubbles are trapped and form the nuclei of the cell structure of the final product. The yeast cannot create the bubbles (Baker and Mize 1941), but it does expand the air bubbles with carbon dioxide, and the dough rises.

The optimum level of mixing in the CBP varies according to the type of flour being used. An energy input of 11 Wh/kg has been found to be a suitable value to achieve optimum dough development for a wide range of flours. However, it is not unusual for bakeries to be mixing to 13 Wh/kg if they are using a particularly strong flour.

Important processing parameters influencing dough quality

Partial vacuum

It is common practice with CBP batch mixers to mix the dough under a partial vacuum during the second half of the mixing. A vacuum level of about 0.5 bar absolute (0.5 bar below atmospheric pressure) produces bread with a finer and more even crumb cell structure than that of bread produced by mixing at atmospheric pressure or above in the same machine. Pulling a vacuum reduces the void fraction of air in the dough from approximately 8 to 4% at the end of mixing. The vacuum level should not be set too high or air will be prevented from being trapped in the dough, and a normal bubble structure will be absent, resulting in bread of very coarse structure.

When pulling a vacuum, at least 50% of the watt-hours used should be under atmospheric conditions, and the vacuum should be pulled halfway through the mixing cycle (Campbell and others 1998).

Positive air pressure

Mixing at pressures greater than atmospheric increases the volume of air incorporated during mixing, which in turn increases the "average" size of the gas bubbles. Mixing under positive pressure allows the baker to choose the type of bubble structure required for different types of bread. A baguette, for example, should have an open and random crumb structure, and mixing under positive pressure allows this to be achieved.

When mixing under positive pressure, a slight reduction in the recipe water may be necessary, as more air in the dough tends to make the dough feel softer. By reducing the water a manageable dough consistency is achieved, and this will help the dough to process through the plant.

Pressure-vacuum mixers have the ability to work at pressures above or below atmospheric conditions in any number of sequences. For a typical sandwich loaf, mixing may be performed under pressure during the first half of mixing, ensuring full utilization of the ascorbic acid, before moving to a lower pressure to complete the process to achieve a close, even crumb structure in the baked bread.

Processing time

Doughs made using the CBP are generally warmer and contain more yeast than those made in the bulk fermentation process, which means it is important to control processing times. Any delays in process will affect the crumb structure and create variability in the quality of the bread. Keeping this in mind, the baker should only produce batch sizes that can be processed through to final proof within 15 min. This is particularly important in the production of standard sandwich bread, which is characterized by a fine even crumb cell structure. If, however, you are producing bread that requires an open crumb structure such as

rolls, buns, and in particular, French-style breads, longer processing times at the intermediate proof stage will help to achieve this; these times can be increased to 20–30 min.

Dough temperature

Dough temperature is important no matter what bread production method is being used. Dough temperature influences the rate of both chemical and enzyme reactions. A low temperature slows the reaction rates, whereas high temperature speeds them up.

A dough temperature of 30–32 °C from the mixer is recommended for no-time doughs (Spiral and CBP). However, during the intense mixing of the no-time doughs, there is a significant rise in dough temperature; depending on the mixer, this can range from 10 °C up to 14 °C for high-speed mixers. Hotter doughs can be softer and stickier, which may limit the amount of water being added and will affect the yield per batch.

Dividing

Dividing the dough needs to be done quickly and with as little stress placed on the dough as possible. Most dividers work by using the dough volume to give a specific weight; it is very important to present a consistent dough to the divider because otherwise underweight or overweight bread will be produced. This affects not only the weight of the dough but also the settings on the final molder, as these have been adjusted to accommodate variations in specific volume. It also affects the legal requirements for bread weight. Too large a volume of dough can cause excess pressure during molding and burst bubbles, which will lead to streaking in the crumb, as discussed earlier.

First molding

Initial shaping of the dough before intermediate proof is used to provide a uniform shape that is then presented to the final molder. Uneven presentation of the dough piece to the final molder can result in loss of loaf volume, grey streaking in the crumb, and misshapen loaves that will cause problems during packaging.

Intermediate proof

An intermediate proof period is recommended after dividing and first molding. This resting period allows the dough to relax before the final molding stage. If the dough is not allowed to relax there is a greater possibility of damaging the bubble structure and thus producing streaking and loss of volume in the baked loaf.

The length of this rest period is flexible. Generally speaking, it should not be shorter than 4 min or longer than 10 min for standard bread, but there are some bakeries that will have intermediate proof times as low as 30 s. A rest period of 15–20 min is recommended for bread varieties characterized by an open, uneven crumb cell structure, such as French-style breads.

Final molding

The function of the final molder is simply to shape the dough piece as required for the bread variety being produced (see Figure 28.2). The molder should be adjusted to achieve the desired shape with a minimum amount of pressure and stress on the dough.
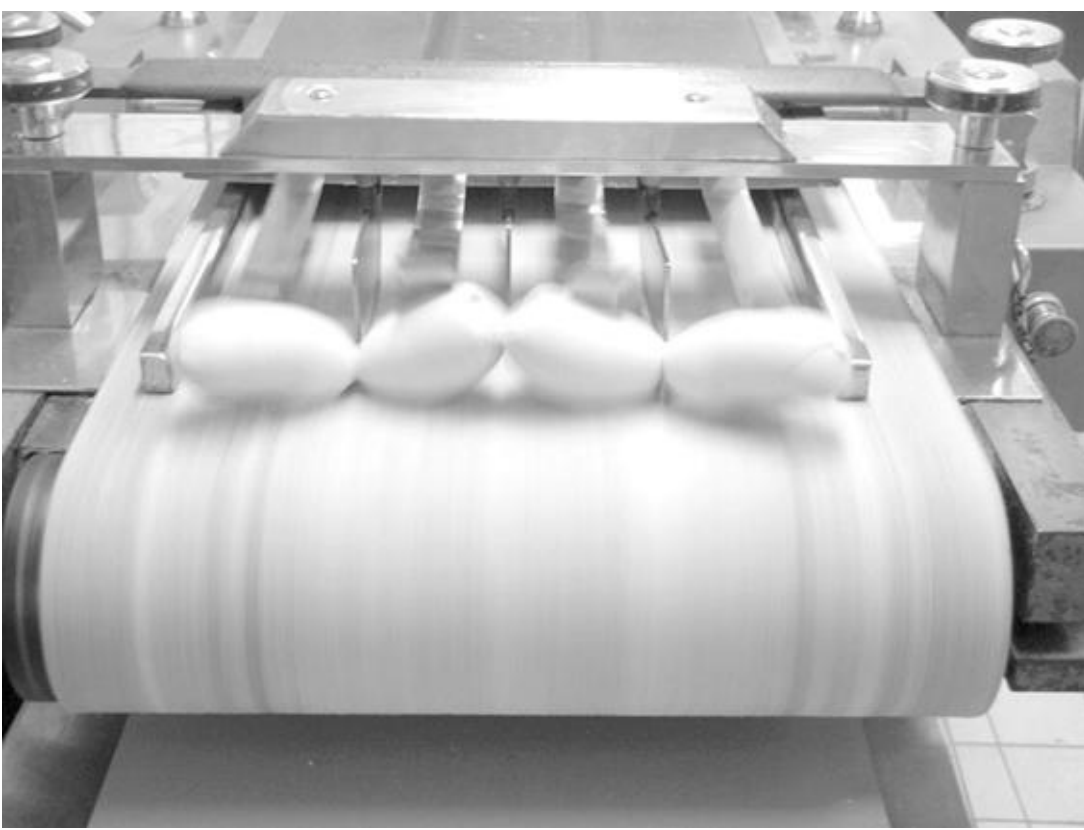
Figure 28.2 Final molder—four-piece. Courtesy of Campden BRI.

Excess pressure during molding may results in damage to the gas bubble structures in the dough, as discussed previously (see streaking).

Final proof

The final proof time can be adjusted over wide limits by varying yeast levels and final proof temperatures. In practice, proof temperatures of 35–43 °C and a relative humidity of 80–85% are commonly used. These humidity levels ensure that the dough does not lose moisture and form a skin on the surface that will produce a dull surface appearance.

Common bread faults and techniques for measuring bread quality

From the craft bakers who produce for the community through to the plant bakeries who engage in mass production, all bakery enterprises have their place in the baking industry. There is a wide range of processing methods used, some of which have been discussed earlier. Examples include sourdough, overnight sponges, bulk fermentation, and mechanically developed dough to name but a few.

The type of bread usually associated with the CBP would be the square sandwich loaf. However, plant bakeries do sometimes use other methods of production to produce the variations that the marketplace now demands. For the purposes of this chapter, plant production will be associated with mass-produced breads and automated processing. Craft breads would usually be associated with crusty, oven-bottom breads that include the majority of hands-on production, such as bloomers, coburgs, and baguettes.

Each type of bread possesses a number of characteristic features that are associated with quality (Figure 28.3). Sandwich bread should have an even, close crumb structure with a thin soft crust, whereas baguette production needs to deliver a random and open crumb structure and an "egg shell" crisp crust. Any deviation from these characteristics will be judged as poor quality.

Figure 28.3 Examples of typical bread varieties found in Europe. Courtesy of Campden BRI.

Bread faults

Loaf quality is not the exclusive responsibility of the baker; it is a team effort. To achieve the desired product quality, the baker relies not only on the quality control and technical

expertise of his ingredient suppliers and the engineering skills of machinery manufacturers, but also on wheat breeding and fundamental research.

Faults still occur, however, and it is important to identify the source of the problem as quickly as possible to avoid problems further along the supply chain. Bread faults can be divided into two broad categories: external (those that affect the external quality of bread) and internal (those that affect the bread crumb properties). External bread faults are those visible on the crust such as blisters, cracks, or sidewall collapse. Internal faults are all those associated with the crumb structure, where one needs to slice the bread to discover the fault.

External quality factors

The British 800 g white pan loaf is a useful example for showing the benefits of quality control. It accounts for the sales of almost 50% of all UK bread: about 5 million 800 g white loaves are sold daily. Not all of the 800 g white loaves are made to the same specifications. The differences shown in Figure 28.4 can be linked to the choice of ingredients, the recipe balance, and the technical ability of the bakeries involved.

Figure 28.4 Examples of U.K. 800 g sandwich bread. Courtesy of Campden BRI.

Loaf volume

Loaf volume is a good indication of the gas retention properties of the dough. It is an indicator of how good the flour protein is and how efficiently the baker has developed the gluten and balanced the recipe and processing requirements.

Low loaf volume can be due to either gas production or gas retention problems. Gas production is linked to yeast activity. As yeast is a living organism, it requires food and warmth to multiply and to produce carbon dioxide, which is required to expand the dough piece. There are ingredients that will retard or kill yeast activity, such as preservatives, salt, and high levels of sugar. Insufficient damaged starch within the flour (reducing the availability of fermentable sugars) will also retard yeast activity. Yeast can also exhibit reduced activity if it has been stored incorrectly.

The gas retention properties of the dough are linked to the ability of the gluten structure to retain the carbon dioxide produced by the yeast. There are several factors that adversely affect the gas-holding properties of gluten. These include (i) low protein levels in the flour, (ii) poor dough development, (iii) lack of oxidation, and (iv) cold or tight (incorrect consistency or rheology) doughs.

Low volume can also be linked to cold final proof conditions or a short final proof. Underproved bread can be identified by "cracking," which may appear on the surface of pan breads or on the lower third of oven-bottom breads or rolls (see [Figure 28.5](#)).

(a)

(b)

Figure 28.5 "Cracking" due to underproof. Courtesy of Campden BRI.

Excessive loaf volume is also a quality issue that causes problems during the packaging and transportation stages of production, as well as sidewall collapse. Excessive volume can be linked to:

- the protein level in the flour being too high;

- excessive yeast or an imbalance of yeast, salt, and improver;
- high dough temperature;
- high final proof temperature;
- excessive final proof time, possibly due to delays in processing;
- excess dough scaling weight;
- small baking tins, which will give the appearance of excessive volume; and
- low baking temperature, which will cause the yeast to continue producing carbon dioxide for longer than required before being killed.

A combination of any of the above will compound the problem.

Oven-spring

Another quality factor related to bread is oven-spring. It is a measure of the rise of the bread in the oven during baking. This can be measured simply by measuring the height of the bread after baking; assuming that the bread has been proved to a standard height, the difference is the oven-spring. Oven-spring is a good quality attribute when it is controlled, but uncontrolled oven-spring has a detrimental effect on finished bread quality. Excessive oven-spring can lead to "flying tops," where the top crust will detach itself from the main body of the loaf (Figure 28.6).
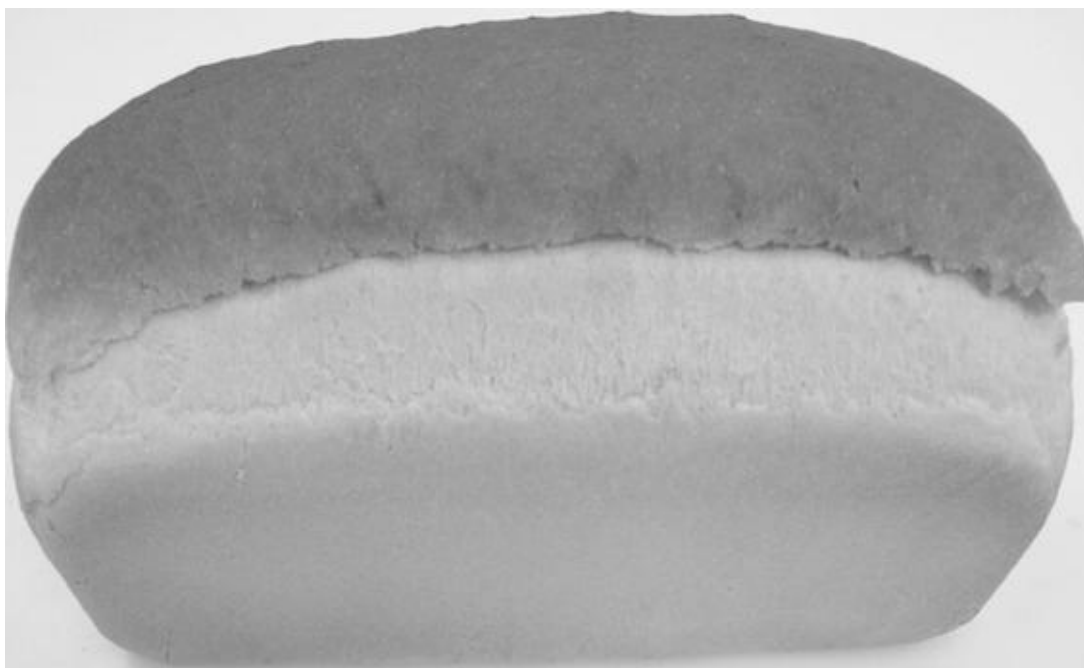
Figure 28.6 An example of a "flying-top." Courtesy of Campden BRI.

Surface blisters

Thin-walled blisters on the surface of the baked bread indicate dough with poor gas retention properties. The blisters may not be visible until after baking, but in extreme cases the blisters will be visible at the end of the final proof. This is sometime referred to as "fat failure" and relates to the type and level of fat being used, especially in no-time doughs, where the property of the fat is a key issue. The fat helps to stabilize the bubbles within the dough; the critical time for this is at the end of final proof, during the transfer to the oven and at the

beginning of the baking stage, when the bubbles are expanding at their fastest. At this stage the crystalline fraction of the fat is thought to align at the surface of the air bubbles and impart stability to the expanding bubbles. If all the fat has melted by the end of final proof, this stabilizing influence is lost. For this functionality, a fat with a slip point in the temperature range 38–45 °C is used, allowing a fraction of the fat to remain solid in the dough at the end of final proof (which is carried out at between 38 and 43 °C).

The level of fat addition will change depending on the flour characteristics; however, a level of 1% for white bread and up to 4% for whole-meal bread is not uncommon. In brown, whole-meal, germ, and multigrain breads, the fat levels are increased because the non-functional parts of the flour, such as the bran, will cause greater bubble instability in the dough. In addition to blisters there may also be reduced loaf volume and possibly no oven-spring, and the internal crumb structure may show some compact areas that appear to be firm to the touch.

Cutting

After the final proof, some styles of bread are cut on the surface. This is sometimes seen as part of the identification of the product, the UK bloomer bread (a hearth bread type) being a typical example of this practice. However, this is not the only reason the dough surface is cut before baking.

- Cutting increases the surface area, which allows for a greater heat transfer into the dough. When producing oven-bottom breads cutting is very important, as there is no tin to hold the shape, and a quick heat transfer is essential to reduce the risk of flowing. Examples of this include Coburgs and bloomers.

- Cutting releases any tension in the dough and creates regions of "weakness" to facilitate dough expansion when it is put into the oven. The region where the cut is made allows a degree of control over the position of the oven-spring in the loaf.

- It is recognized that flavor is more intense in the crust. Cutting of the dough helps to increase the crust area, and this has a beneficial impact on the finished taste and crustiness of the bread. Cutting is not easy and is recognized as a great skill. The difference between a product that has been cut well and one that has not is clearly demonstrated in Figure 28.7.
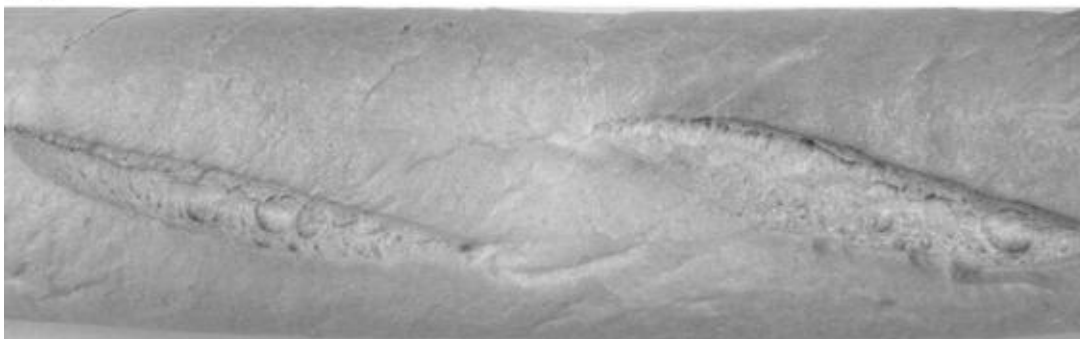
Figure 28.7 Cuts on the surface of French baguettes. (a) Good example; (b) poor example. Courtesy of Campden BRI.

Crust and crumb color

The crust color is highly dependent on the time and temperature of baking. The components of the ingredients used in the formulation are also important. Flour plays an important role in the perceived color of both the crumb and crust of a loaf. The grade color of the flour will influence the crumb color of the bread. Grade color is dependent on the extraction rate and the amount of chemical bleaching given to the flour (this is no longer permitted in Europe). The use of soy flour can also affect crumb color as it contains the enzyme lipoxygenase, which reacts with the carotenoid pigments in the flour to produce a bleaching effect. The amount of damaged starch in the flour plays an important role in the extent of color development in the bread crust. If flour contains low amounts of damaged starch, there may only be sufficient sugars released by the action of α-amylase for yeast fermentation and little or no sugar left for the Maillard reaction to produce crust color during baking. This scenario would be more likely in bulk-fermented doughs and in doughs that have undergone excessive proof than in no-time doughs. On the other hand, if there are high levels of damaged starch, there will be excessive levels of sugars released, which will cause high coloring of the crust. Other ingredients that can affect crust color are the inclusion of milk powder or sugar in the recipe. High α-amylase levels (for example, low Hagberg falling number) in the dough will also break down the damaged starch, resulting in high residual sugar levels and high crust color.

Internal quality factors

The bubble structure that is generated in the dough during the mixing stage is dependent on the style of bread that is being produced. Baguettes, crusty rolls, and ciabatta all require an open irregular crumb, whereas sandwich bread requires a close even crumb structure. The

crumb structure obtained will be dependent on the type of mixer used, the recipe formulation, atmospheric conditions at the end of mixing, bulk fermentation time, intermediate proof time, and final molding. It must always be borne in mind that the bubble structure at the end of mixing begins to expand shortly after it leaves the mixer, and all subsequent processing stages are designed to preserve and reorient the bubbles.

Open random structure

This type of crumb structure may be required if producing ciabatta, but even then the amount of openness must be controlled so as not to cause weakness within the crumb (Collins 1983). Generally speaking, in all processes, an open crumb structure is an indication that too much gas has been produced during the final stages of processing. This can come from:

- an imbalance in the recipe formulation between the yeast and the salt, sugars, or preservatives (which will affect the amount of carbon dioxide produced by the yeast);
- incorrect vacuum level being pulled when using CBP or finishing the mixing at the wrong atmospheric pressure;
- too high a dough temperature (encouraging the yeast to work quickly); or
- delay after mixing and before final molding (with no-time dough, the period of time between the scaling and final molding stage should be no longer than 10 min, and usual times are around 4–6 min).

Cell wall thickness

As the dough is processed after mixing, the aim is to maintain the bubble structure that has been developed, but the subsequent processing can damage these bubbles. The damaged bubbles will coalesce and produce areas in the crumb that look grey and dull and are firm to the touch. Small shallow air cells with thin cell walls reflect the light more efficiently, thus producing a whiter crumb; as the cell walls thicken, for example due to insufficient oxidation/development or damage to the bubbles, the color of the crumb becomes grey. When the bubbles burst, they merge into one larger bubble with thicker cell walls. The thickness of the wall influences both visual and eating qualities:

- thicker cell walls give a grey looking crumb;
- thick cell walls give a firm feel to the crumb, thus influencing perceived shelf-life;
- thin cell walls give better reflection of light and thus a whiter looking crumb.

Damage to the bubbles can be traced back to the final molding, where the dough is sheeted, rolled, and elongated either to be cut into four pieces, as in sandwich bread, or a single piece, as for the production of farmhouse bread or bloomers. Figure 28.8 shows examples of the four-piece and single-piece molding.
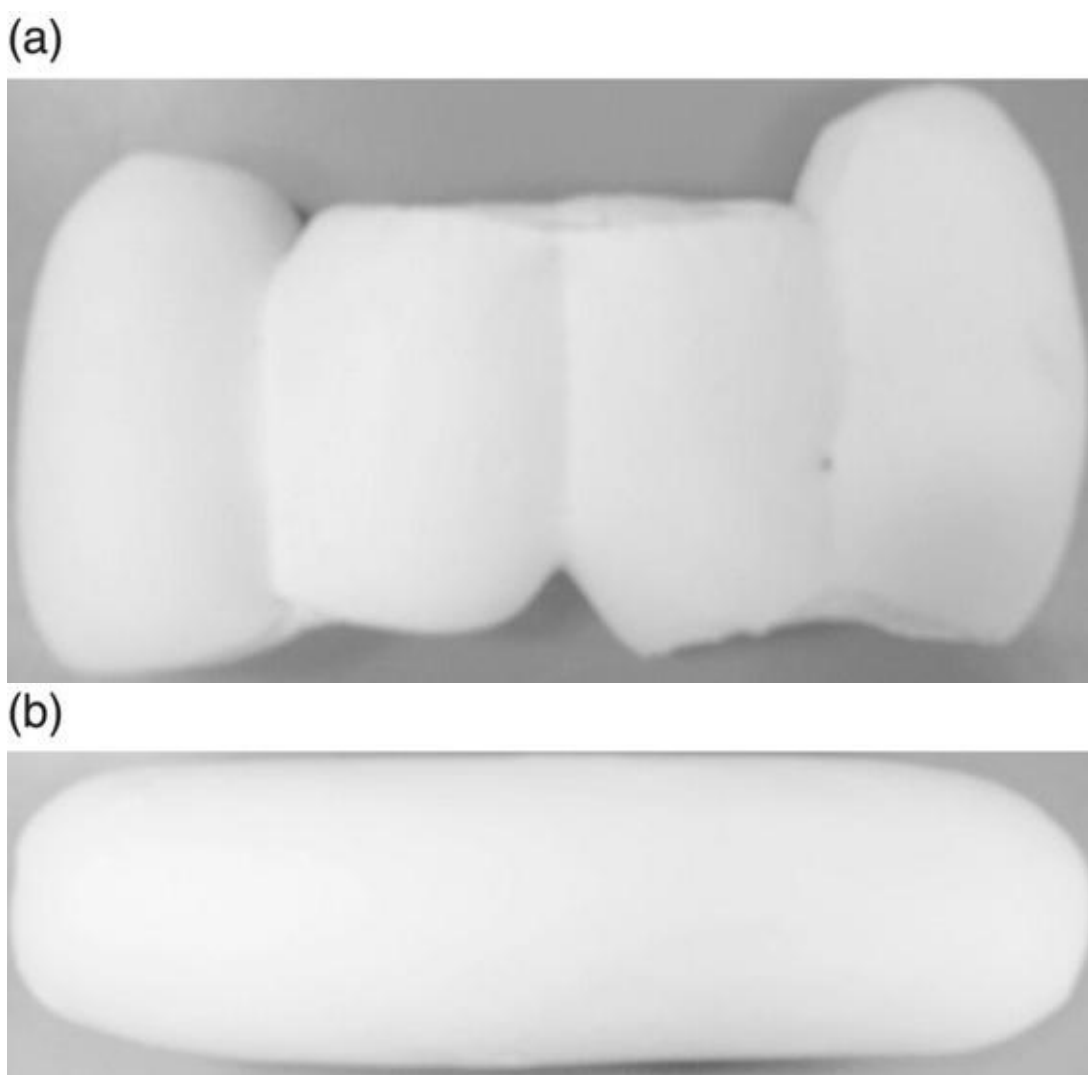
Figure 28.8 Examples of four-piece (left) and single-piece molding (right). Courtesy of Campden BRI.

Excess pressure during processing will burst the bubbles. For example, having the rollers set too closely may produce grey horizontal areas running along the base of the slice. Having the guide bars set too closely will give vertical grey areas in the crumb, but these will only be visible in the end slices of the loaf.

Holes

There are many types of hole that appear in the crumb, some due to the dough not being able to adhere together after curling, and others that appear due to weaknesses within the dough due to ingredients or processing.

Holes along the molding lines can be associated with (i) inadequate pressure being applied by the pressure board, (ii) dry surface due to skinning, (iii) excessive divider oil, or (iv) excessive dusting flour.

A *"handbag fault"* is a hole at the top of the loaf, 2–3 mm directly under the crust, that is not a blister. It appears as though the crumb has fallen away; although the surface of the hole is usually smooth, the position is always the same. This fault can be linked to excessive levels of fungal α-amylase or the addition of malt flour to the recipe. The problem may appear worse if the dough has skinned or if it is handled heavily during the transfer from the prover to the oven.

Holes in the bottom third of the loaf can be a regular occurrence in sandwich breads. They can run the length of the bread, appearing as a triangular void. Usually this type of hole is related to heat transfer during baking being too quick, which can be linked to worn bread pans. As the pans are transferred around the plant, the first areas to be worn are the bases, which means that the heat can transfer into the dough too quickly. Therefore, rather than the dough expanding gradually, the dough breaks and holes are formed. The problem can be made worse by:

- hot tins – the loaf may also show dark brown scorch marks on the side; in extreme cases these scorch marks can be white, when the yeast is killed as soon as it touches the pan, and the "dead" area is pushed away from the tin as the dough expands;
- bread pans not being greased or the insides of the pan being rough, acting like sandpaper and resisting the dough as it tries to expand up the bread tin;
- tight dough;
- excessive molding at the sheeting stage of the final molder;
- low humidity in the final prover, which dries the surface of the dough and restricts its growth before baking.

Measurement of bread quality

The quality criteria of all types of bread need to be established to determine whether they are acceptable to the consumer. The more commonly used characteristics related to bread quality are loaf volume, crumb color, and crumb quality. These measurements are routinely combined with texture measurements using texture analyzers.

Loaf volume measurements

The volume of an individual loaf is typically assessed by a seed displacement method in which the product displaces a volume of seed equivalent to its own volume. The method uses a container of known volume that is calibrated by rape or pearl barley seeds, employing a dummy loaf of known volume. For a bake trial it is recommended that an appropriate number of loaves be tested and limits set for the weight of the seed that is collected for each replication.

Other methods of measuring loaf volume include the use of image analysis and methods employing ultrasound and laser light. Image analysis allows the volume of a sliced loaf to be determined by performing measurements on the cross-sectional areas of a number of slices taken from selected places along the length of the loaf and combining these measurements with the known length of the product (Cauvain 1998). More recent developments use ultrasound (Girhammar 2002) and laser sensors that move in a semicircle as a loaf rotates on a skewer passed centrally along the length of the loaf. This measurement is rapid compared with the seed displacement method, taking less than a minute to perform, and is less operator dependent.

Crumb color measurements

Instrument-based measurement of the color of bread can be made using colorimeters that are designed to characterize the color of a surface by three parameters in a number of color

spaces. This tristimulus method uses complex mathematical transforms to generate values in three spectral ranges, X, Y, and Z. The Y value can be taken as a measure of bread crumb whiteness. Typically the loaf is cut in half, the measuring head of the colorimeter is placed against the exposed crumb, and measurements are obtained in triplicate.

Crumb quality

The judgment of crumb quality at the point of bread manufacture is typically performed subjectively by the baker who takes into account the number, size, and distribution of the bubbles and the thickness of the walls between the cells and decides whether the quality is acceptable or not. However, recent developments in the techniques of image analysis have lead to opportunities to measure crumb cell structure objectively and rapidly, allowing crumb quality assessment to be performed in greater detail and with better accuracy. Calibre Control International, in partnership with CCFRA Technology, Ltd., has developed a system called C-CELL. It is a dedicated system that produces high-resolution images of bread and other baked goods so that individual cell patterns can be quantified. Crumb cell analysis quantifies the cell distribution and the size and number of cells in a slice of bread.

Texture measurements

Texture profile analysis is used for the objective measurement of bread texture. It is a rapid method and is particularly suitable for use in quality control. The principle of objective texture measurement can be described as the science of deforming objects and monitoring their response. There are numerous texture analyzers suitable for measuring the texture of bread and bread products. Typically, an instrument will consist of a flat platform and a probe, usually positioned above the platform attached to a moveable arm. The arm can be positioned precisely and moved up and down at a controlled speed.

A sample, which could consist of a circular disc cut out of a slice of bread or a whole slice of bread, is placed on the platform and compressed to a specific distance using a suitable probe. The test produces a force–time graph that represents the magnitude of the resistance of the sample to deformation. The sample may be either compressed once or compressed twice by moving the probe up and down twice in rapid succession. A typical graph of a texture profile analysis, which is characterized by two compressions, is shown in Figure 28.9. The graph consists of two peaks, each corresponding to one of the successive compressions. Typically the second peak is a little smaller than the first as a result of damage to the bread crumb structure by the first compression, and that allows the crumb structure to be compressed more easily by the second compression. There are a number of textural parameters that can be obtained from the force–time graph. The parameters and their significance are covered in detail elsewhere (for example, Bourne 1990; Cauvain 1991), so only a basic explanation is offered here. The most relevant feature for determining quality is the firmness of the bread crumb, and this is obtained from the maximum force (F_1) of the first force peak of the first compression. Another property of interest is how much the bread crumb recovers after it has been compressed, that is, the springiness, which can be obtained by finding the ratio (T_2/T_1) of the time taken to reach the second peak (T_2) to the time taken to reach the first peak (T_1). The areas under the first and second peak also provide useful information about the ability of the crumb to withstand compression. This ratio of the integrated area of the second peak divided by the area of the first peak is called the cohesiveness of the crumb.
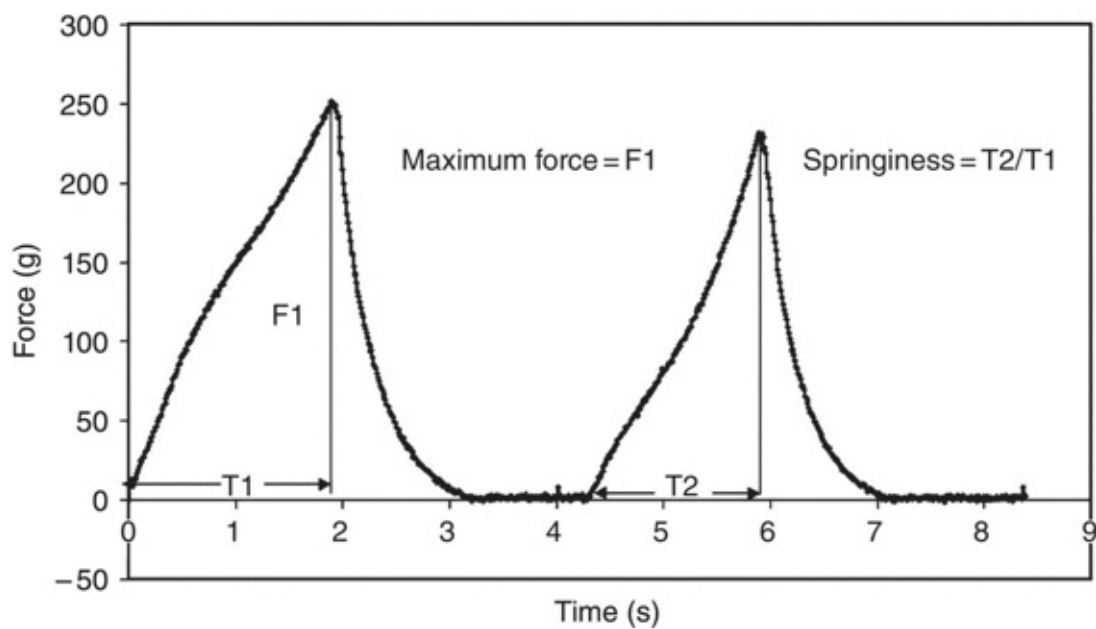
Figure 28.9 An example of the graph obtained from a texture profile analysis test.

The properties of the crust, in particular, the crispness of the crust, also influence the eating quality of bread. The strength of the crust and hence its crispness can be evaluated using penetrometry, again using a texture analyzer. This procedure can be carried out on the whole bread or baguette, and the force required for a cylinder to penetrate through the crust is recorded. The maximum force recorded relates to the thickness of the crust, a thicker crust producing a higher peak force. The highest peak height would be expected of freshly baked bread, with moisture changes after baking making the crust softer and leathery if the product is packed in an environment where it cannot lose moisture.

Factors influencing bread staling and the use of additives to improve perceived freshness

The eating quality of bread begins to change soon after baking, the quality usually deteriorating with time. This has been discovered from numerous studies involving both instrumental texture testing and sensory testing of stored bread (Setser 1996; Zobel and Kulp 1996). With time, bread becomes firmer, and bread was judged to be stale by a sensory panel as the firmness increased. There is, therefore, a correlation between the firmness of the bread and the sensory perception of its freshness. It is therefore important to keep the bread soft for it to be perceived as fresh by the consumer for longer.

The deterioration processes affect both the crumb and the crust, but in different ways. There are two main changes that are thought to be responsible for the loss in eating quality: (1) loss of moisture from the loaf and (2) the migration of moisture from the crumb to the crust. The bread also increases in firmness with time, and this is thought to be largely due to the changes in the degree of crystallinity in the starch fraction. There are also other changes such as the loss of aroma and flavor that, combined with other changes, make the bread unacceptable to the consumer. Bread staling is a wasteful process. It is therefore not unsurprising that there is considerable interest in the bread industry in finding ways to slow down the rates of the various firming processes, so that the bread can be perceived as fresh for longer.

Craft breads are often eaten soon after purchase, but sandwich bread would be expected to last 3–5 days. However, consumer pressure for bread with an ever-longer shelf-life has seen products that can stay soft and mold-free for up to 12 days. In this section, the influence of factors such as loaf specific volume and temperature on the firming properties of bread is examined, and the ingredients and methods available to the technologist to extend the shelf-life of bread are reviewed.

The effect of loaf specific volume on bread staling

The quantitative relationship between loaf specific volume and the rate of staling, as measured by changes in crumb firmness, has been investigated in great detail, covering a range of flour properties, a number of additives, and baking and storage conditions (Axford and others 1968; Elton 1969). The results showed that loaf specific volume was a major factor influencing both the rate and degree of staling, both of which decreased in a linear manner, over the range studied, as loaf volume increased.

The general understanding is that any factor that lowers the specific loaf volume of bread increases the staling rate. The converse is also true – any factor that improves the specific volume helps to reduce the rate of staling. The influence of the effects of loaf volume is important. When assessing the effectiveness of a particular additive as an antistaling agent, it is important to demonstrate whether any beneficial effect is due to an incidental increase in loaf specific volume (due to the additive) or to a specific effect independent of the loaf volume. The beneficial effect of many so-called antistaling agents and processing methods can be explained by their incidental effect in improving loaf volume. However, additives that have been identified as independent of this factor include the enzyme maltogenic α-amylase,

which has been demonstrated to possess strong antistaling properties, and emulsifiers such as glycerol monostearate.

The practical implications of the influence of loaf specific volume on bread staling can be utilized by the baker in various ways but has obvious limitations. The British public has a distinct preference for the denser more traditional product, and an increase in specific loaf volume may produce an unacceptable product.

The bread making process itself can also have an influence on the rate of staling. For example, the use of the CBP usually leads to an increase in loaf specific volume (other things being equal) and hence a reduction in the rate and extent of staling. It has been demonstrated that the reduction in the staling rate of bread made by the CBP is an inherent feature of the process and not just a reflection of increased specific volume. The conclusion was reached from the observations that the rate and extent of staling of CBP bread varied less with changes in specific volume than that in bread produced by the bulk fermentation process (BFP). The underlying reason for the differences in behavior could be that the limiting firmness of the CBP bread was lower than that of the BFP bread at a given specific volume. Using differential scanning calorimetry, it was confirmed that the limiting endothermic peak values were significantly larger for BFP bread than for CBP bread.

The effect of temperature on bread staling

The rate of staling of bread during storage is highly dependent on the temperature of storage postbaking. The rate of bread crumb firming is fastest at temperatures close to 4 °C, decreases at temperatures below and above 4 °C (Kent and Evers 1994; Colwell and others 1969), and falls to virtually zero when the bread is frozen. It was shown that for any given bread stored at different temperatures, over the range 21–32 °C, the value of the limiting crumb modulus remained constant. The value of the rate constant was also shown to decrease with increasing storage temperature over the same range. This meant that no matter what the storage temperature was above the freezing point of bread, the bread tended to reach the same limiting firmness, though the rate decreases as the temperature increases. The fact that the staling rate constant has a negative temperature coefficient strongly indicates that a physical process such as crystallization is the major factor involved in increasing the crumb firmness. However, it was shown that the increase in crumb firmness of bread stored at 43 °C was greater than would be predicted on the basis of starch crystallization. This raises the possibility that other mechanisms are also responsible for additional increases in firmness at high storage temperatures (Willhoft 1973).

It is well known that if stale bread is heated to a center crumb temperature that is close to the temperature at the end of baking, the crumb firmness returns to its original value and staling proceeds again at the normal rate (Zobel and Kulp 1996). If the temperature attained is lower during reheating, then the original firmness may be obtained, but the loaf firms more quickly thereafter. Note that reheating bread using a conventional oven results in considerable moisture loss, and the loaf may become unacceptably dry for eating.

The effect of additives

Ingredients such as fat and emulsifiers, generally regarded as antistaling agents, often produce an increase in loaf volume, and this would then be expected to result in lower

firmness initially and throughout its shelf-life. However, increasing loaf specific volume is not always desirable for commercial reasons. It is therefore important to evaluate whether an ingredient can produce a decreased rate of staling independent of its effect on volume. Both emulsifiers and enzymes have been claimed to act as antistaling agents in bread. However, at this stage a distinction must be made between ingredients that actually slow that rate of firming and those that simply soften the bread crumb without affecting the rate at which a loaf firms with storage. Such materials produce a loaf with low initial firmness, and the firmness stays low throughout the shelf-life of the loaf.

Emulsifiers such as distilled monoglycerides, diacetyl tartaric acid esters of mono- and diglycerides, and sodium steroyl-2-lactylate are likely to act as antistaling agents through one or more of three mechanisms: (1) they can improve crumb softness by increasing loaf volume; (2) they can interfere with the rate and/or extent of starch crystallization; (3) the amylose−emulsifier complex formation can slow down the crystallization of the amylopectin, thus reducing the initial and final firmness of the loaf. The distilled monoglycerides, particularly those with saturated fatty acids with chain lengths in the range C_{16} to C_{18}, are known to act as crumb softeners through the third mechanism. Many studies have shown that the amylose fraction of the starch is fully retrograded by the time the loaf is cooled to ambient temperature and that increasing crumb firmness is due to the slower process of amylopectin crystallization (Russell 1983; Krog and others 1989).

Enzymes

Enzymes have a long history of being used as antistaling agents. Claims of antistaling effects have been made for all the α-amylases, including the bacterial, fungal, maltogenic, and even the cereal types, but not for cereal β-amylases. Similar claims have been made for hemicellulases and lipases. For several of these enzymes, there are conflicting reports about whether they possess true antistaling properties. It is likely that some of them simply soften the bread by increasing loaf volume. Such effects may be useful in commercial practice to give an improvement in the perceived freshness to the consumer, provided there is a minimum firmness and resilience in the fresh bread for handling and slicing.

Amylases hydrolyze starch polymers when the starch granules are hydrated and swollen, as they are after gelatinization or damage by milling. All types of α-amylases act on starch as it swells in water at about 65 °C.

Fungal amylase is an endo-acting enzyme that attacks starch chains randomly, producing large dextrins and thinning starch viscosity to improve loaf volume. It is rapidly destroyed at 70−75 °C and has no significant antifirming effect other than that caused by increased loaf volume.

Cereal amylase is also endo-acting and has a similar action to that of fungal amylase, causing damage to starch granules and leading to dough softening. It has greater thermostability, being destroyed at 80−85 °C. If present at too high a level it can lead to a sticky crumb lacking in resilience. There are some reports of an antistaling effect, but this may be confused with the softening of the crumb.

Maltogenic bacterial amylases act as exo-enzymes (working along the chain of the starch molecules) and produce small sugar molecules such as maltose and maltotriose. This group of amylases has a large antistaling effect and is reported to reduce the rate of starch

crystallization (Si 1998). These amylases seem to maintain crumb resilience, which can be a problem with excessive use of crumb softening emulsifiers, and are destroyed in baking by 85 °C and therefore would not be expected to cause problems with crumb stickiness.

The hemicelluloses of wheat consist of a mixture of polysaccharides, arabinoxylans, arabinogalactans, and β-glucans. These materials are found in the cell wall material of wheat endosperm and are present at high levels in the bran tissues. White flour may contain 2–3% of this material, of which the soluble portion (about one-third) is known as pentosans and the remaining portion is water insoluble aggregates. Of particular interest is the reported powerful effect they have on water binding and gluten development in the dough. Endo-acting hydrolytic *hemicellulases* can degrade the aggregates by splitting the polysaccharide chains, so that the insoluble material becomes soluble, and their water-binding capacity is reduced. The result, similar to that produced by α-amylase, is a softer dough that can expand more in the oven and produce a larger loaf volume. However, excessive enzyme activity can produce dough stickiness. A secondary benefit of the enzyme action on the insoluble aggregates is an improvement in the performance of the flour proteins. The conversion of the insoluble fraction into smaller molecular size allows the gluten to have better gas-holding and extensional properties during oven-spring, resulting in improved loaf volume. The best effects are seen with endoxylanases, and pure forms of some enzymes are commercially available.

The 1,3-specific *lipases* cleave the bond between the fatty acid esters and glycerol, producing a mixture of fatty acids and monoglycerides. It is claimed that the monoglycerides produced may be used to replace added monoglycerides (Christiansen and others 2003). This would depend largely on the triglyceride being attacked. Saturated fatty acids with chain lengths of 14–18 carbon atoms are the most effective antistaling monoglycerides (Russell 1983). They function by forming complexes with amylose molecules, and this helps to reduce the rate at which amylopectin molecules retrograde and increase the firmness of the bread crumb. In commercial practice, monoglycerides are added at concentrations of 0.5–1.0% flour weight. It has not been established whether added lipase can produce the amount of monoglycerides required to obtain the necessary antifirming properties in bread.

The benefits of an antistaling agent to the loaf can be classed into two main categories:

1. A reduction in the crumb limiting firmness would be of commercial importance, as the actual rate of crumb firming would be reduced. A softer loaf is perceived to be fresher by the consumer compared with a firmer loaf. This would not necessarily have an effect on the rate of staling.

2. The more fundamental action of the additive on the actual rate of crystallization of the starch molecules would reduce the rate of staling. The addition of α-amylase to reduce the rate of staling falls into this second category, as does the effect of storage temperature.

When evaluating potential ingredients as antistaling additives, an assessment of the beneficial effect resulting from an incidental increase in loaf specific volume should be made. It must also be noted that the baking test itself has inherent variability and that it would be necessary to perform several replicate experiments to demonstrate true antistaling properties. Analytical techniques such as differential scanning calorimetry can be used as a rapid testing method, however, and this method has the advantage of being independent of

loaf volume. The effect of loaf specific volume can be removed by the use of techniques such as differential scanning calorimetry and differential thermal analysis to evaluate the effectiveness of antistaling additives on the rate and extent of crystallization of starch in bread.

Recent developments and future prospects

The role of ingredients and methods of dough mixing have a large impact on bread quality. New developments employing combinations of pressure and vacuum can be used to create a whole range of bread crumb features that encompass a variety of different bread types. Using the same ingredients, a number of different bread types can be produced by changing the dough mixing methods. However, the critical feature to achieving the desired quality of the final product is actual control of the mixing process so that dough development is complete.

Various techniques to control the quality of bread dough have been explored. Rheological properties help to determine dough quality during mechanical handling and to predict bread performance (Stojceska and Butler 2012). Correlation between the rheological properties and the baking performance is proposed to depend on the characteristics of flour and its protein content as well as the type of rheological test applied. Some specific instruments have been developed for the characterization of large-deformation properties of dough such as the Farinograph, the Mixograph, the Extensograph, and the dough inflation system. In particular, the Farinograph and the Mixograph measure the torque profile generated during mixing. Large-deformation rheological tests showed a better discrimination of baking performance than fundamental rheological methods (Dobraszczyk and Salmanowicz 2008). It was demonstrated that three large deformation rheological tests – the Kieffer dough extensibility system, the D/R dough inflation system and the Mixograph test – produced a positive correlation with the bread volume (Dobraszczyk 1997, 1999).

However, all the physical measurements that describe the rheological properties of dough cannot fully predict its baking quality. Why this should be so is not clear, but it may be a consequence of what the tests actually measure. Rheology-based methods measure protein–protein interactions, which create a three-dimensional network of gluten. Hence, it is the strength of these interactions that is being measured. A study reported that the gliadin : glutenin ratio of flour has a correlation with the rheological properties of dough and bread quality (Barak 2013). The glutenin subunits can be quantified by using sodium dodecyl sulphate polyacrylamide gel electrophoresis (SDS-PAGE) and allele-specific polymerase chain reaction (PCR) (Ram and others 2011). The near-infrared (NIR) technique has also been examined for use in obtaining more information about the chemical changes that take place in the dough during mixing (Alava and others 2001). NIR energy is absorbed by the OH groups in water and by peptide bonds between amino acids in proteins at specific wavelengths. There is a correlation between the molecular analysis results produced by NIR reflectance spectroscopy and the dough rheological properties determined by alveograph (Arazuri and others 2012).

There is considerable interest in understanding what becomes of the bubbles that are in the dough before proof and after baking. Do all bubbles survive during proof and the baking process and appear as holes in the bread crumb? One of the problems experienced with studies involving dough is the fragility of the dough as it undergoes proof. The challenge has been to study bubble development during proving without damaging the cell structure by using a non-invasive technique. Campden and Chorleywood Food Research Association (CCFRA) have used a medical X-ray CT scanner to obtain images of dough during the proving stages, and some answers are now emerging about the behaviour of bubbles (Joppen 2003;

Whitworth and Alava 1999). The connectivity of cell structure in bread was also successfully visualized in three dimensions through X-ray tomography images (Wang and others 2011). Indeed, image analysis of dough using magnetic resonance imaging (MRI) has also become popular due to its non-invasive nature and relatively high spatial resolution. The acquired images can be used to analyze dough pore distribution, dough volume, and bread crust thickness (Bajd and Serša 2011). Use of advanced image analysis techniques is continuing to improve our understanding of the influences of factors such as wheat varieties, recipe formulations, and mixing conditions.

The consumer's demand for healthier products drives the innovations in producing healthier bakery products. Bread has an advantage as it can be used as a medium to carry some functional ingredients. Modifications of bread ingredients are made to enhance the nutritional values of bread. Novel flour and traditional grains have been substituted into the bread formula, such as amaranth (Sanz-Penella and others 2013) and oat, spelt, rye, and buckwheat (Angioloni and Collar, 2011a) as a multigrain blend, to improve the nutritive values of bread. Also, there is a growing trend of fortifying bread with phytochemical-based ingredients. These ingredients enhance the nutritional quality of bread (such as protein, mineral, antioxidant, dietary fibre fraction, and resistant starch) and lower the amount of digestible starch in bread.

Developing bakery ingredients for people with special dietary needs are also of increasing concern. Barley and oat-based bread containing soluble dietary fiber (β-glucan) helps to reduce the total cholesterol (TC) but not change the blood glucose level (Tiwari and Cummins, 2012). Bread supplemented with omega-3 fatty acid has been produced commercially throughout the world, with a claim that it increases the amount of high density lipoproteins (HDL) and reduces the level of triglycerides (Hayta and Ozugur 2012). A type of reduced-caloric density, high-fibre bread was created by adding hydrocolloids and prebiotic oligosaccharides (Angioloni and Collar, 2011b). This product offers a higher amount of resistant starch and a lower amount of digestible starch, which is connected to the lowering of the glycemic index tested *in vitro*.

A longer shelf-life of bread is highly desired by the modern bakery industry to meet the consumer's demand of convenient bakery products. Frozen dough technology can reduce the problem of having bread staled by making fresh bread available at anytime of the day. Frozen dough can be used to increase the shelf-life of bread up to 12 months. A variety of processes to make frozen dough can be applied, including fully baked frozen bread (FBF), partially baked frozen bread (PBF) and bread from unfermented frozen dough (UFD). Improving the quality of frozen dough is still being discussed and studied to grow the market of this product (Rosell and Gomez 2007). Incorporating the dough with hydrocolloids, emulsifiers, oxidants and cryoprotectants (Minervini and others 2011), enzymes such as glucolipase, hemicellulase and hexose oxidase (Almeida and Chang 2012) or soy proteins (Simmons and others 2012) have been reported to be able to improve the quality of frozen dough.

The shelf-life extension of bread is closely related to its packaging, which functions to minimize some reactions due to the contact of bread with water vapour and oxygen in the environment. Modified atmosphere packaging (60% CO_2, 40% N_2) was applied to extend the shelf-life of bread with acceptable sensory quality up to 24 days at 20 °C (Fik and others 2012). Active packaging can also be applied to improve the shelf-life of bread, for example by applying ethanol emitters and oxygen absorbers (Latou 2011).

Consumers are also showing concern about the nature of the ingredients that are included in a recipe to improve the quality of bread. The enzyme lipase was shown to improve bread quality attributes (bread volume and texture) and it could be used to replace some chemical emulsifiers such as diacetyl tartaric esters of mono-glycerides (DATEM) (Moayedallaie and others 2010). Claims are that the action of the enzyme, in situ, generates materials that are more surface active than the substrate material. This offers an opportunity to either eliminate or reduce the use of added emulsifier and thus remove the need to declare additives on the packaging. The importance of this development is highlighted by a marked increase in the sale of organic bread products, which will continue as the range of breads produced is increased. The negative response of the consumer to products labelled as organic is being replaced by a realization that the quality parameters by which an organic product should be judged are different from those applied to bread produced with traditional ingredients.

Bread producers are also faced with the situation whereby popular dietary trends, such as the Atkins diet, are forcing the industry to rethink recipe formulations to produce acceptable alternatives. The challenge of producing such a (low carbohydrate) loaf is an interesting one, since carbohydrates play such a vital role in building the structure of bakery products.

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29
Sourdough

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Introduction

Sourdough is generally regarded as a mixture of cereal flour and water fermented with lactic acid bacteria (LAB) with or sometimes without yeasts. However, there is currently no official definition of sourdough. In the narrowest sense, sourdough refers to sour fermented dough used as a leavening ingredient in bread making. In the broadest sense, sourdough may encompass fermented cereal foods. Therefore, sourdough may exist in various physical forms – solid (or firm), semi-solid and liquid (or fluid). In the context of this chapter, the broad definition of sourdough is adopted to reflect the diverse range of cereal foods fermented with LAB with or without yeasts.

Traditionally sourdough is prepared from flours of wheat, rye or a mixture of both for making sourdough bread, especially in European and Northern American countries. Nonetheless, in other parts of the world, fermented cereal foods are commonly produced from flours of other cereals such as rice, maize, sorghum, and millet, in addition to wheat and/or rye. Thus, the definition of sourdough in this chapter also includes sourdoughs derived from flours of other cereals, besides rye and wheat.

Sourdough fermentation entails the growth and metabolism of LAB which enable dough acidification and matrix transformation. Hence, the focus of this chapter is placed on the impact of LAB on sourdough attributes in relation to flavor, texture, biopreservation, and nutritional enhancement. Detailed information on other aspects of sourdough is available elsewhere (Hansen 2004, 2012; Meuser and Valentin 2004; Diowksz and Ambroziak 2006).

Microbiology and starter cultures

The microflora of sourdoughs usually, although not always, comprises LAB and yeasts, especially for spontaneous sourdoughs. The cell populations of LAB and yeasts in sourdoughs are generally at levels of 10^8–10^9 and 10^6–10^7 colony-forming units per gram, respectively, and as such, the ratio of LAB to yeasts is broadly 100 : 1 (Hansen 2004, 2012).

The LAB species isolated from sourdoughs are those from the genera *Enterococcus, Lactobacillus, Lactococcus, Leuconostoc, Lactococcus, Pediococcus*, and *Weissella*, but the dominant LAB species and strains involved in sourdough fermentations are lactobacilli (De Vuyst and Neysens 2005; Weckx and others 2010; Hansen 2012). Typical sourdough lactobacilli include *Lb. sanfranciscensis, Lb. brevis, Lb. buchneri, Lb. fermentum, Lb. reuteri*, and *Lb. plantarum*. New species of LAB have been isolated from sourdoughs and are also typically lactobacilli such as *Lb. mindensis, Lb. panis, Lb. pontis, Lb. rossiae*, and *Lb. zymae* (De Vuyst and Vancanneyt 2007; De Vuyst and others 2009).

The yeasts in sourdoughs are dominated by species from the genera *Candida* and *Saccharomyces*, although yeast species from other genera such as *Issatchenkia, Hansenula*, and *Pichia* are occasionally found. The common sourdough yeasts are *C. humilis* (physiologically closely related *C. milleri*), *S. cerevisiae*, and *S. exiguus* (De Vuyst and Neysens 2005; Hansen 2012).

Yeasts are inevitably associated with LAB in the complex sourdough microbial ecosystem and metabolic interactions between them evolve as a result. The yeasts release nutrients such as amino acids and vitamins that are beneficial for growth of the nutritionally fastidious LAB (Gobbetti 1998), which in turn produce acids and reduce pH to the optimum value of about 5 for yeast growth during early stages of sourdough fermentation. The classic metabolic interaction between *Lb. sanfranciscensis* and the maltose-negative sourdough yeasts such as *C. milleri* has been well described in the sourdough literature (Gobbetti 1998; Hansen 2012). In essence, the lactobacillus converts maltose via intracellular maltose phosphorylase into glucose-1-phopshate and free glucose; the latter is then excreted into the sourdough to be utilized by the maltose-negative yeasts such as *C. milleri* and *S. exguus*. This unique metabolic relationship is sometimes erroneously referred to as "symbiotic" in the literature, because the lactobacillus and the yeast can grow independently of each other. The conversion of maltose via maltose phosphorylase into glucose-1-phopshate and free glucose is energetically advantageous for the lactobacillus without energy (ATP) expenditure. In addition, the association of maltose-positive yeasts such as *S. cerevisiae* and LAB in sourdoughs seems to be stable and non-competitive, even though they compete for the same growth substrates, presumably due to the abundance of fermentable carbohydrates (maltose, glucose and fructose) (Venturi and others 2012).

The sourdough environment is acidic with a final pH as low as 3.5. This acidic condition is harsh for the survival and persistence of LAB, although they are regarded as aciduric. In fermented milk systems with a pH of 3.5–4.0, it has been demonstrated that the survival of probiotic and non-probiotic LAB can be enhanced by yeasts, in spite of being yeast–LAB combination dependent (Liu and Tsao 2009a, 2010a). By analogy, the associations of sourdough yeasts and LAB may be beneficial for the survival and persistence of the latter, but evidence is required.

Sourdough fermentation can occur spontaneously, relying upon the naturally present or so-called wild microflora in the flour and from the environment. However, spontaneous fermentation is not consistent, difficult to control, and may result in poor-quality sourdoughs or may not even take place. Industrial sourdough processes entail the use of starter cultures to enable better control of consistency, efficiency, and quality.

Sourdough starter cultures can be undefined or defined. The composition of undefined starter cultures is unknown (for example, mother sponge of a mature sourdough used for back-slopping). The defined starter cultures consist of known pure single or mixed LAB strains and yeasts (for example some commercial cultures of *C. humilis, C. milleri, S. cerevisiae, Lb. sanfranciscensis, Lb. brevis, Lb. plantarum*). As such, sourdoughs can be classified into three types, type I (a, b, c), type II and type III (De Vuyst and Neysens 2005), which are summed up here.

Type I sourdoughs are prepared with traditional methods using pure or undefined cultures. Type Ia starter preparation contains pure *Lb. sanfranciscensis*, maltose-negative yeasts *C. humilis, C. milleri*, and/or *S. exguus* derived from natural sourdough fermentations. Type Ib sourdough starters consist of various partially defined lactobacilli and *C. humilis*. Type Ic sourdoughs are produced at higher temperatures (> 35 °C) with partially defined *Lb. fermentum, L. reuteri, Lb. amylovorus*, and yeast *I. orientalis*.The starter cultures of type II sourdoughs are composed of partially defined mixed lactobacilli without yeasts for liquid sourdough fermentation with a high acid content of pH < 3.5. Type III sourdoughs are dried sourdoughs fermented with defined mixed cultures of *Lb. brevis, Lb. plantarum*, and *Pc. pentosaceous* without yeasts.

Sourdoughs fermented with LAB only usually serve as dough acidifiers (type II) or as acidifier supplements (type III) or as aroma carriers (type III) in sourdough bread making (De Vuyst and Neysens 2005; Brandt 2007) or are directly consumed as cereal foods. (Salovaara and Simonson 2004; Guyot 2012).

Microbial physiology and metabolism

LAB strains including those isolated from sourdoughs can be broadly classified into two categories – homofermenters (obligate or facultative) and heterofermenters (obligate or facultative) – based on their glycolytic pathways of hexoses. The homofermenters convert hexoses to predominantly lactate (> 90%) while the heterofermenters catabolize hexoses to lactate (about 50%), ethanol, acetate and CO_2 (Liu 2003, 2012). The so-called facultative heterofermenters are also known as facultative homofermenters that ferment pentoses with the production of lactate and acetate, relative to the obligate homofermenters that do not utilize pentoses. The obligate heterofermenters also ferment pentoses to lactate and acetate. In the presence of additional electron acceptors such as fructose, the obligate heterofermenters reduce fructose to mannitol and produce extra acetate and ATP, while mannitol can be fermented to lactate by facultative heterofermenters such as *L. plantarum*. The detailed pathways of carbohydrate fermentation by LAB are described in several reviews (Liu 2003, 2012; Gänzle and others 2007).

Some LAB including sourdough strains can degrade citrate and form acetate, lactate, diacetyl, CO_2, and succinate (Liu 2002; Gobbetti and others 2005; Gänzle and others 2007). The catabolism of citrate requires the presence of a fermentable sugar and as such, the co-metabolism of citrate and sugar can result in the formation of additional acetate and ATP (Gobbetti and Corsetti 1996).

Sourdough LAB possess proteases, peptidases, and amino acid converting enzymes, which break down cereal proteins with the production of peptides and amino acids as well as transform amino acids to various volatile and non-volatile compounds that impact on the taste, aroma, and health attributes of sourdough products (Gobbetti and others 2005; Gänzle and others 2007, 2008; Rizzello and others2008). The transformation of branched-chain and aromatic amino acids to volatiles in LAB usually occurs by transamination, which requires the presence of an amino acceptor, preferably α-ketoglutarate. The transamination of amino acids in sourdough lactobacilli, which are mostly obligate heterofermenters, seems to be different from that of homofermenters in meat and dairy fermentations. The sourdough lactobacilli utilize α-ketoglutarate as an electron acceptor, converting it to 2-hydroxyglutarate; to use α-ketoglutarate as an amino acceptor, amino acids in excess and additional electron acceptors such as citrate are required (Zhang and Gänzle 2010). This implies that addition of α-ketoglutarate to the fermentation matrix may not be an effective option to boost aroma compound formation in sourdoughs, unless the requirement for extra amino acids and electron acceptors is met.

Arginine can be degraded by LAB to ornithine, ammonia, ATP, and CO_2, following the arginine deiminase (ADI) pathway, with or without the production of citrulline (Liu and Pilone 1998). Some strains of sourdough LAB such as *Lb. sanfranciscensis* CB1, and *Lb. fermentum* IMDO 130101 can catabolize arginine via the ADI pathway, which enhances their stress resistance and persistence in the acidic environment of sourdoughs due to ammonia (and pH rise) and ATP production (De Angelis and others 2002; Gänzle and others 2007; Vrancken and others 2009).

Glutamate, together with glutamine, is a major amino acid in cereal proteins and its

concentration increases or decreases during fermentation due to proteolysis and glutamine deamidation, depending on LAB species and strains, because some LAB strains are able to convert glutamate to γ-aminobutyric acid (GABA) and CO_2 (Rizzello and others 2008, 2010; Stromeck and others 2011). Glutamate decarboxylation confers acid resistance to LAB and enhances their survival as a result of pH increases (Su and others 2011). In addition, thiol accumulation due to glutathione reduction by strain-specific sourdough LAB confers oxygen tolerance and protects them against oxidative stress during fermentation (Jänsch and others 2007; Gänzle 2009).

Exopolysaccharide (EPS) production seems to be characteristic of sourdough LAB, although this feature is also strain-dependent. Sourdough LAB species and strains typically synthesize exocellular homopolysaccharides composed of one type of monosaccharides such as glucans (for example dextran) and fructans (for example levan) using glycosyltransferases with sucrose as the glycosyl donor (Tieking and Gänzle 2005). Sourdough lactobacilli produce both glucans and fructans (Tieking and Gänzle 2005), whereas sourdough LAB of *Leuconostoc* and *Weissella* genera tend to produce dextrans (Bounaix and others 2009; Katina and others 2009; Galle and others 2010). Some strains of *Leuconostoc* and *Weissella* also produce oligosaccharides such as glucooligosaccharides and isomaltooligosaccharides that may act as prebiotics (Katina and others 2009; Galle and others 2010). EPS may benefit sourdough products by improving water absorption and retention, enhancing dough rheology and stability as well as increasing bread loaf volume and delaying bread staling (Tieking and Gänzle 2005). Microbiologically, EPS may enhance bacterial tolerance to low pH of sourdough, for example *L. reuteri* (Kaditzky and others 2008).

Flavor and texture

Flavor compounds in sourdoughs and fermented cereal foods are derived from the flour matrix (for example via lipid peroxidation), fermentation by LAB and yeasts (generating flavor compounds and flavor precursors) and the thermal process (for baked goods) (for example Maillard reaction and caramelization), involving both chemical and enzymatic reactions (Hansen and Schieberle 2005; Salim-ur-Rehman and others 2006; Gänzle 2009). The final composition of flavor compounds is a net balance of biotransformation, chemical transformation, and physical losses during heat treatment.

The characteristic sourness of both taste and odor of sourdough products and fermented cereal foods is imparted by lactate and acetate, both of which are generated by LAB during fermentation. A balanced flavor should have a molar ratio of lactate to acetate of approximately 4 : 1 (Hansen 2004). The sourdough LAB strains contribute to acidification while the yeasts are largely responsible for aroma compound formation. To achieve a balanced flavor, a combination of homo- and heterofermentative LAB strains should be part of the starter culture mix, where the homofermenters produce lactate and the heterofermenters generate both lactate and acetate. The facultative heterofermenters may be used due to their ability to produce acetate from pentoses (Gobbetti and others 2000). The production of acetate may be accentuated by selecting citrate-positive LAB strains, by adding pentosans and pentosanases, or by adding citrate and/or fructose (Gobbetti and others 2000, 2005; Gänzle and others 2007).

The aroma compounds of sourdoughs and fermented cereal foods are composed of a diverse range of volatiles, such as acids, aldehydes, alcohols, esters, ketones, and sulfur compounds, besides acetate. The contribution of sourdough LAB to aroma is more than just the formation of acetate; they also produce aldehydes, alcohols, esters, and diacetyl. Nevertheless, sourdough yeasts are the major contributors to aroma compounds with the production of a much wider range of volatiles at higher levels (Hansen and Schieberle 2005; Salim-ur-Rehman and others 2006; Ravyts and De Vuyst 2011). Heterofermentative sourdough LAB strains are capable of reducing the flour-derived character-impact odorants aldehydes to their corresponding alcohols, decreasing their potency and flavor intensity; these alcohols may act as precursors to esters (Gänzle 2009; Ravyts and De Vuyst 2011).

Arginine catabolism by some strains of sourdough LAB results in the production of ornithine, which is a precursor to 2-acetyl-pyrroline with a roasty aroma formed during baking, and may improve the sensory properties of sourdough bread crust (Gobbetti and others 2005; Gänzle and others 2007). Further, strain-dependent deamidation of glutamine to glutamate by sourdough lactobacilli may contribute to the savory (umami) taste (Stromeck and others 2011; Su and others 2011).

Fermentation of LAB has a significant impact on the rheological and textural characteristics of firm sourdoughs and this impact is dependent on process variables such as flour type, LAB strains, and fermentation conditions. The impact of sourdough on wheat and rye bread texture has been discussed in detail by other researchers (Hansen 2004, 2012; Arendt and others 2007) and is summarized here. Acidification associated with LAB fermentation partially inactivates endogenous flour α-amylase activity and limits excessive starch hydrolysis, decreasing solid dough stickiness. In rye dough rich in pentosans with a high

water-binding capacity, the dough viscosity decreases due to pentosan degradation by pentosanase activity during the early stages of fermentation. Acidification considerably inactivates pentosanase activity and restricts pentosan degradation, minimizing viscosity reduction. The acidic environment of sourdough also enhances solubility and swelling of pentosans, which are beneficial for dough rheology and bread texture. The gluten protein network is transformed at low pH due to increased positive net charge and gluten protein becomes more solubilized, which facilitates proteolysis by proteases with acidic pH optima and thus, weakening dough stability.

In addition to the consequential viscoelastic impact of proteolysis, starch hydrolysis, and pentosan degradation, EPS produced *in situ* by sourdough LAB has a positive effect on dough rheology and bread texture through increasing water absorption, improving dough machinability and loaf volume as well as retarding bread staling (Tieking and Gänzle 2005; Arendt and others 2007). On the other hand, the glutathione reductase activities in sourdough LAB strains increase the amounts of thiol, which participates in the thiol–disulfide bond exchange reactions, resulting in gluten depolymerization and dough softening (Jänsch and others 2007; Gänzle 2009).

Biopreservation

Sourdough breads and fermented cereal foods are susceptible to microbial spoilage, especially fungal spoilage. LAB are known to produce antimicrobial metabolites, for example, short-chain fatty acids, antimicrobial peptides, phenyllactate, 4-hydroxy phenyllactate, diacetyl, hydrogen peroxide, bacteriocins, lactic and acetic acids; some of these are antifungal, such as phenyllactate, 4-hydroxy phenyllactate and acetic acid (Gobbetti and others 2005; Schnürer and Magnusson 2005; Gänzle 2009; Rizzello and others 2011). The concentrations of individual antimicrobial compounds produced may be low, but they function in synergy to contribute to the biopreservation of sourdough products.

Sourdough yeasts may also contribute to biopreservation. Some yeasts are mycocinogenic by producing mycocins ("killer toxins") that are antagonistic towards other yeasts, which are exploited in alcoholic beverage fermentations. Other yeasts are used as biocontrol agents against molds on postharvest fruits. Two yeasts, *Debaryomyces hansenii* and *Williopsis saturnus*, have been shown to inhibit the growth of a range of yeasts and molds in fermented milks (Liu and Tsao 2009b, 2010b). Indeed, a recent study showed the anti-mold activity of an antagonistic yeast, *Wickerhamomyces anomalus* (formerly *Pichia anomala*) in sourdough bread (Coda and others 2011). Caution must be exercised when selecting antagonistic yeasts as biocontrol agents against molds in sourdough products to avoid inhibiting the growth of the desired sourdough yeast cultures.

Process parameters

Sourdough production is influenced by four critical factors, namely flour type, flour extraction rate, flour/water ratio (water content), fermentation temperature and time, and the amount of starter cultures or mother sponge (Hansen 2004, 2012; Decock and Cappelle 2005). Sourdoughs can be prepared from a variety of cereal flours, though wheat and rye flours are the most common; other cereal flours such as rice, millet, sorghum, and maize can also be used. Flour extraction rate refers to the yield of flour obtained from a cereal after milling. Flour with a high extraction rate has a higher nutrient content and a higher buffering capacity, which in turn affect the sourdough fermentation process and acidification. Flour/water ratio (water content) determines the consistency and dough yield (DY, the quantity of dough attained in kilograms per 100 kg of flour). The consistency of dough ranges from being firm (low DY) to liquid (high DY), which also affects dough acidification and aroma compound formation. The impact of temperature and time on sourdough fermentation varies with sourdough starter cultures, whereas the inoculum size of starter cultures determines fermentation time and the speed of acid production. The practical aspects of sourdough process control have been discussed in detail elsewhere (Hansen 2004, 2012; Decock and Cappelle 2005).

Nutritional enhancement

It is now recognized that sourdough fermentation enhances the nutritional status and health benefits of sourdoughs and fermented cereal foods. Nutritional enhancement is achieved through gluten reduction, improved mineral bioavailability via phytate degradation, biofortification with vitamins and bioactive compounds, retarded starch digestibility and lower glycemic responses, and biosynthesis of oligo- and polysaccharides with prebiotic properties for beneficial gut microbiota (Katina and others 2005; Poutanen and others 2009). Further, sourdough fermentations improve antioxidant activity, inhibit lipid peroxidation, and decrease antinutritional α-galactooligosaccharides such as stachyose and raffinose (Songré-Ouattara and others 2008; Đordevic and others 2010; Rizzello and others 2010).

Sourdough LAB possesses proteases that degrade wheat protein, gluten, which causes celiac disease in gluten-intolerant people and this creates an opportunity to develop gluten-free cereal products using sourdough fermentation technology (Gobbetti and others 2007; Gänzle and others 2008; Moroni and others 2009). Phytic acid is an anti-nutritional factor in cereals by binding minerals such as Mg^{2+}, Ca^{2+}, Fe^{2+}, and Zn^{2+}. The higher phytase activities of sourdough LAB enable the dephosphorylation of phytic acid to form myoinositol and phosphoric acid, decreasing or eliminating the capacity of phytic acid to chelate minerals, thus enhancing mineral bioavailability (Gobbetti and others 2005). Further, the acidic environment of sourdough is conducive to the activities of yeast and endogenous cereal phytases (Poutanen and others 2009). Indeed, a mice study demonstrated that sourdough bread improved the iron status of mice relative to yeast bread and bread without starters (Chaoui and others 2006).

Fermented cereal foods

Among the sourdough products, wheat and rye sourdough breads are the most well known and well studied, especially in Europe and North America, as evidenced by the ample amount of literature in this field. In other parts of the world such as Asia and Africa, however, there are numerous fermented products derived from cereals other than wheat and rye, such as rice, maize, sorghum, and millet (Nout 2009; Rhee and others 2011; Guyot 2012). In these products, LAB fermentations play a crucial role and yeasts may or may not play significant functions, depending on their cell populations. Fermentations fundamentally transform these cereals into more functional and nutritional foods with respect to aroma, taste, texture, nutrient bioavailability, and health benefits (Nout 2009; Rhee and others 2011; Guyot 2012).

The traditional Chinese steamed buns (breads), with or without fillings, are produced mostly from wheat flour sourdoughs fermented with LAB and yeasts either spontaneously or using mother doughs (Keeratipibul and Luangsakul 2012). The mother dough starters consist of a range of LAB and yeasts, dominated by lactobacilli (typically *Lb. plantarum* and *Lb. casei*) and *S. cerevisiae* (Luangsakul and others 2009; Zhang and others 2011). Another wheat-derived fermented food is tarhana, which is a wheat flour–yoghurt mixture and is fermented with yoghurt bacteria (*Lb. bulgaricus* and *Strepcococcus thermophilus*) and baker's yeast (*S. cerevisiae*) (Bozkurt and Gürbüz 2008).

There are a number of fermented rice products throughout the world. Fermented (sour) rice noodles, which are popular in the South and Southwest of China, are produced by natural fermentation involving mainly LAB and back-slopping (Yang 2012). The dominant LAB species are *Lb. plantarum* and *Lb. cellobiosus*, and yeast contribution is limited because of the low cell counts (Lu and others 2008a). The role of natural LAB fermentation is mainly to improve texture (for better chewing quality) by modifying the amorphous region of starch granules (purer rice starch obtained), and for removing chemical components of low molecular weights (Lu and others 2005, 2008b). Liquid sourdoughs of rice flour may also be subjected to steaming to produce rice cakes (Kelly and others 1995; Rhee and others 2011) or baking to make gluten-free cereal products (Meroth and others 2004). Other fermented rice foods with ingredients such as wheat flour and legume include dosa, idli, and selroti, which are prepared from liquid sourdoughs after fermentation with LAB and yeasts (Soni and others 1986; Yonzan and Tamang 2010).

Various fermented cereal foods derived from millet, maize, and sorghum exist throughout the world. The common feature of these fermented cereal foods is acid fermentation using LAB, and yeasts may contribute to leavening, flavour or even alcoholic content. These foods may serve as beverages, porridges, gruels, cooked doughs, steamed cakes, breads or food ingredients. Detailed information is described elsewhere (Thapa and Tamang 2004; Nout 2009; Guyot 2012).

Future research

There is a need to develop novel starter cultures for sourdough and cereal fermentations for speed of fermentation, cost reduction, biopreservation and shelf-life extension, and flavor and functional enhancement. The use of amylase-producing LAB strains would accelerate fermentation and decrease costs where exogenous amylase addition is practiced (Sanni and others 2002). The application of kefir grains containing both LAB and yeasts as sourdough cultures yields a firmer texture, higher moisture content, lower acidity, and longer freshness of baked sourdough products (Plessas and others 2005), presumably in part due to EPS produced by LAB strains in the kefir grains. Indeed, development and utilization of EPS-producing LAB strains is one of the emerging fermentation technologies for the creation of innovative and functional baked sourdough products (Tieking and Gänzle 2005; Arendt and others 2007; Lacaze and others 2007). The incorporation of mycocinogenic yeast strains as sourdough cultures may reduce fungal spoilage (Liu and Tsao 2009b, 2010b), which merits exploration.

Beyond the traditional sourdough breads, it may be necessary to develop novel sourdough products as functional ingredients for convenient applications, including dried sourdoughs, pasty sourdoughs, liquid sourdoughs, dough acidifiers, and aroma carriers (powder, liquid/pasty forms) (Brandt 2007). Liquid sourdoughs can be pumped allowing easier operation and automation, and meeting the demands of modern bakeries (Carnevali and others 2007, 2012). However, the physicochemical environment of the liquid sourdoughs such as redox differs from that of the firm sourdoughs and this may affect the growth and metabolism of sourdough starter cultures such as fermentation time, acidification, and flavor compound formation. For instance, an overproduction of odor-active isovaleric acid by *Lb. sanfranciscensis* and *S. cerevisiae* was observed in liquid sourdough, but not in solid sourdough (Guerzoni and others 2007). This area warrants further study.

Cereals are a suitable medium for developing functional foods. This can be achieved by fermentation with probiotics and by biofortification (Salovaara and Simonson 2004; Hugenholtz 2008). Indeed, fermented cereal food may be a good delivery vehicle of probiotics in places where consumers are averse to milk products (Salmeron and others 2009; Rathore and others 2012). Probiotic fermentation of cereals may be performed together with selected low ethanol-producing yeasts to improve flavor and probiotic viability, as some yeasts have been shown to produce pleasant aroma compounds and enhance probiotic viability in fermented milks (Liu and Tsao 2009a, 2010a).

It is also possible to develop functional sourdoughs and fermented cereal foods rich in GABA, a bioactive compound with multiple physiological functions such as lowering blood pressure. Glutamate is a major amino acid in cereal proteins and its concentration rises or falls during sourdough fermentation due to proteolysis and glutamine conversion (Gobbetti and others 2005; Gänzle and others 2007, 2008; Gänzle 2009) as well as LAB variations in converting glutamate to GABA (Rizzello and others 2008, 2010; Stromeck and others 2011). This offers an opportunity to enrich the GABA content of sourdoughs and fermented cereal foods by selecting LAB strains that transform glutamate to GABA and incorporating them in the starter culture mix.

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30

Frozen Dough and Par-baked Products

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Introduction

Milling and baking are among the oldest technologies known to humankind. Bread represents one of the oldest "convenience" foods and its production and consumption has spread to most parts of the world. Bread making has moved from small-scale, local production to large-scale industrial production. In part this change has arisen to cope with the increasing demand for bread and other bakery products. While per capita consumption of bread in highly industrial countries has continued to slowly decline (Rosell 2003) the position in developing countries is commonly one of increasing consumption with "traditional" westernized bread products becoming the "new" products in developing regions.

A key quality driver for the purchase and consumption of bread is its "freshness". This concept is not an easy one to define since it requires consideration of both crumb and crusts properties. What is perhaps easier to define is the concept of bread "staling", that is the loss of those "just-baked" qualities of bread which commonly include a soft and slightly chewy crumb texture (Cauvain and Young 2006a). Unfortunately the nature of bread crumb (and crust) changes once bread has left the oven and begun to cool. The main changes in character are associated with increasing firmness and progressive increase in fragility of the crumb. Such changes are related to moisture loss from the product, for example when unwrapped, but are also associated with moisture migration from crumb to crust, for example moisture equilibration if wrapped in a moisture impermeable film, and microscopic changes to the starch and gluten structures.

When baking and shopping purchases are carried out locally and consumption is within 24–48 h after production, these changes do not leave the product inedible. However, if the product is to retain its edibility for longer, then the introduction of strategies which extend the product shelf-life are called for. An alternative to introducing shelf-life extension strategies is to use technology to interrupt standard industrial bread processes and use the intermediates as the basis for bake-off production at local sites such as village bakeries, railway and gas stations, and in retail baking environments. Freezing, refrigeration, and par-baking represent the two most common means of achieving such aims. However, a major challenge for the primary manufacturer of frozen dough and par-baked products is that the ultimate product is only determined at final bake-off and commonly the conditions and practices used at that moment in time are not within the primary manufacturer's control.

Definitions and technologies

There is no clearly defined line between refrigeration and freezing conditions when applied to baked products. This is because the formulation of baked products has a profound effect on the "freezing point". In particular it is the level of soluble solids which has the greatest influence, with the main ones being salt and sugars. Thus the freezing point for bread dough which is low in sugar is much higher than that of an unbaked cake batter for example. The range of temperatures concerned start at around −5 °C for bread and falls to around −18 °C for cake batters. For the purposes of discussion in this chapter, the dividing line between refrigeration and freezing will be taken as −5 °C.

In the discussions which follow, the relatively poor conductivity of dough and baked products plays a major role in determining the application of freezing and par-baking technologies. Heat can only be removed or introduced into a dough unit through its surface, thereafter conduction is the main mechanism for heat to flow through the dough piece to its centre. Temperature differentials between the product and the ambient air clearly play a significant role in determining the rate of heat flow but the temperature gradient that is set up through the dough piece is equally important. A practical consequence of this – and factors such as yeast activity – are key determinants of final product quality and so freezing and warming conditions tend to be relatively lengthy, often taking hours rather than minutes (Table 30.1). Because of these circumstances, both freezing and par-baking are most successfully applied to smaller units like pastries, rolls, and breads where the dough diameter is relatively small compared with their surface areas, for example French sticks.

Table 30.1 Typical freezing times and rates for frozen dough

Core temperature achieved (°C)	Time taken to cool from 30 °C (min)	Average freezing rate (°C/min)
0	47	0.62
−10	86	0.44
−20	110	0.44

Refrigerated or retarded dough

Refrigeration is used to reduce the activity of yeast in fermented dough thereby prolonging the storage life of the unbaked dough. Bakers most commonly refer to the application of refrigeration as *retarding* and the equipment in which the dough is held as a *retarder*. The main distinction between a refrigerator and a retarder is that the refrigeration coils in the latter are designed with a larger surface area to maintain a higher cabinet relative humidity than would otherwise be possible with a standard refrigerator. This design change is necessary to reduce the likelihood that the stored dough will lose moisture (skin) and consequently yield inferior products. Typically the dough pieces are stored at temperatures between −5 and +8 °C. The lower the temperature, the lower the rate of gas production by the yeast, but even at −5 °C measurable gas production can occur over the 1−3 days that are typical for retarded products.

The retarder may be used alone or be part of an integrated unit known as a *retarder-prover*

which combines cooling, chilled storage, and warming operations. The aim of retarding is to "time-shift" production so that dough may be prepared in advance of the requirement for baking. Retarding is most often seen in smaller and retail bakeries since it allows for dough pieces to be ready for baking when the bakery or store first opens. For the reasons described earlier, retarding is best suited to the manufacture of rolls, buns, and fermented pastries.

Un-proved frozen dough

If longer-term storage of unbaked dough is required then it is necessary to hold it at temperatures which slow down (effectively stop) yeast activity and other physicochemical changes. This commonly means storing the product at temperatures around −20 °C. It is not necessary to have the whole of the dough unit at the final temperature before storage but it is important that all areas of the dough unit are "frozen". Common practice is to use a blast freezer to lower the core temperature of the dough pieces to around −10 °C using air temperatures around −30 °C. Lower air temperatures are not desirable because of the adverse impact on the yeast (see later, Yeast in frozen and refrigerated dough).

Thus when the products enter the storage freezer there is a temperature gradient in the dough pieces but provided the temperature is not allowed to rise, the final stages of freezing can take place in the storage unit without significant loss of quality.

Frozen, non-fermented dough pieces require defrosting and proving before they are baked. These stages have to be carried out gradually to minimize the temperature gradient in the defrosting product in order to optimize final product quality. Defrosting times can be very long and the process is best achieved using specialized equipment. Retarder-provers with a special defrosting stage are often used for the purpose. Once again small products like rolls and buns and small diameter breads are better suited to frozen dough technology.

Pre-proved frozen dough

There are some bakery products which can be proved before being frozen. The objective of the technology is to provide units which can be taken straight from the freezer and placed in the oven for baking, or which only require a short acclimatization period between the freezer and the oven. The application of the technology is currently limited to small items and is especially successful with laminated products as discussed below. Storage time in the deep freeze tends to be limited because the carbon dioxide gas trapped in the dough is prone to leak out and products often collapse in the freezer. Since the temperatures in the freezer will inactivate the yeast in the dough (see later, Yeast in frozen and refrigerated dough) there is no new carbon dioxide gas available to contribute to dough expansion on baking.

Par-baked products

The manufacture of par- or part-baked products is based on the premise of setting the product structure in the oven while minimizing the formation of crust color (Figure 30.1). After storage, the par-baked products are reheated, which refreshens the product and provides the final coloration. Par-baking is often used to deliver a pale, almost white crust color though increasingly for food service environments the products will already be colored, in some cases par-baked products are described as "90% baked" (Bent 2007). Small diameter

products are best suited to par-baking though larger units can be produced. The main challenge is ensure that sufficient heat reaches the centre of the product to achieve refreshening (see later, Impact of reheating (bake-off)). Par-baked products may be stored under ambient conditions but this tends to limit their practical shelf-life because of mold growth and so gas-packed or frozen units are more common.

Figure 30.1 Example of a par-baked product.

Dough gas retention properties

Key to expanding bread dough during proof and the early stages of baking is the improvement of the gas retaining potential of the gluten-forming proteins in the dough before the later stages of processing. The basic mechanism by which this is achieved is commonly referred to as "dough development" (Cauvain and Young 2008). This is an ill-defined and all-embracing term which describes the desirable, composite properties of the gluten network in the dough. Detailed descriptions of dough development and the processes which affect the degree of development can be found elsewhere but a key change is the increase in the strength and extensibility of the gluten network so that it is more able to contain the pressures in the dough which arise from the expansion of the trapped gas bubbles. In the oven, the control of gas bubble coalescence is a key contributor to final bread quality and in this context the role of the gluten network is critical.

Modification of the gluten network, or dough development in baker's parlance, can be achieved in a number of ways. The most common is by leaving the dough after mixing to rest for a period of time, often many hours. This approach is commonly referred to as "bulk fermentation" (Cauvain 2007a) and relies mainly on the natural changes which occur in yeasted dough. An alternative is to use high levels of energy input during mixing to enhance the development of the gluten network, such as practiced in the Chorleywood Bread Process (Cauvain and Young 2006b) and other no-time dough making processes which use mechanical mixing (Cauvain 2007a); in these cases a period of bulk fermentation is unnecessary and processing of the dough can proceed as soon as mixing is finished. Whatever the process used for dough preparation, the underlying principle is that higher levels of flour protein with appropriate quality will yield better dough gas retention and therefore lead to bread of larger volume and improved crumb softness.

In a number of bread making environments, functional ingredients are added to increase the gas retention properties of dough; the most common term for these ingredients is "improvers" (Williams and Pullen 2007). The use of improvers has become common practice in the production of many forms of bread and fermented goods and is particularly important in the context of this chapter as many of the chemicophysical changes which take place in frozen dough processes tend to reduce the ability of the dough to retain gas when it is defrosted ready for baking. As will be discussed, dough processes which rely on extended fermentation periods for dough development are not best suited for freezing though they may be used for refrigerated and par-baked products.

A number of different functional ingredients may be used to improve the gas retention properties of dough. They may be broadly considered under three headings: chemical oxidizing agents, fats and emulsifiers, and enzymes. Details of the associated chemistry of these functional ingredients and their uses in bread making may be found elsewhere (for example Chapters 10, 12, 15, and 16) but references to their application in the manufacture of frozen and par-baked products will be included in the sections which follow.

An understanding of the impact of dough development and the addition of functional ingredients on dough gas retention in refrigerated and frozen dough is vital for ensuring final product quality. Once the dough has entered the freezer nothing can be done to add to its gas retention properties, but a number of changes can occur which could reduce them. The

technology of refrigerated and frozen dough in particular is intended to deliver the dough units for baking without further processing, so it is especially important that the "right" gas retention properties are built into the dough before it is frozen.

Yeast in frozen and refrigerated dough

Yeast is a living microorganism used by bakers for the production of carbon dioxide gas which contributes to the expansion of dough. In dough, yeast is able to produce carbon dioxide gas over a wide range of temperature; peak gas production is at around 40–45 °C and the cells are killed at around 55 °C (Wiggins and Cauvain 2007). As the temperatures approaches 0 °C gas production slows down. Yeast cell viability is affected when dough is frozen and the loss of gas production which occurs as a result is considerable. In addition to loss of gas production, the act of freezing yeast cells in dough induces other important changes which have potential impacts of dough gas retention.

While the freezing point of a yeast cell's cytoplasm is about –1 °C, generally it remains unfrozen and therefore super cooled to –10 or –15 °C, even when ice is present in the surrounding dough (Mazur 1965). Mazur (1970) considered that this indicated that the cell membrane provided an effective barrier against the growth of ice crystals outside of the cell. However, the under-cooled water in the cytoplasm has a higher vapor pressure than the surrounding ice and cells begin to equilibrate with the surrounding dough by losing water through the membrane. At around –15 °C equilibrium is reached and ice crystals begin to form in the cytoplasmic space. Thus yeast damage induced by freezing depends on the manner in which the cells equilibrate their content during freezing and so depends on the rate of cooling. If the cells are cooled slowly, water can leave the cell due to vapor pressure differential with external ice, but with rapid cooling the water does not leave the cell. Dehydration of the cells' contents as ice forms will concentrate the cell solutes which can, in turn, damage the cell membrane. Even if the ice crystals formed during freezing do not rupture the cell membrane, there is a significant risk to membrane integrity when the dough is once again warmed and the ice crystals which have been formed melt. A number of studies have shown that a slow freezing rate is preferable for preserving yeast activity (Lorenz 1974; Neyreneuf and Delpuech 1993; Casey and Foy 1955; El-Hady and others 1996; Harvet and others 2000). However, slow freezing rates increase the exposure of the cells to high solute concentrations with consequent negative effects and so the optimum freezing rate will be one which strikes a balance between the two negative effects; that is, rapid enough to minimize exposure to the high solute concentration effects but slow enough to limit intracellular ice formation. Disrupted yeast cells release proteolytic enzymes and reducing agents, particularly glutathione, which have negative effects on dough gas retention properties (Ribotta 2003). These changes reinforce the need for limiting freezer damage.

Yeast stability in frozen dough is significantly affected by the degree of pre-freezing activity which has taken place. Hino and others (1987) showed that stability was inversely related to the time of active yeast fermentation before freezing. Pre-freezing fermentation makes yeast more susceptible to freeze–thaw damage, not least because cells in active fermentation have a thinner cell membrane (Stauffer 1993). The practical consequence of increased susceptibility of fermenting yeast to freezer damage is that better results are obtained by limiting yeast activity prior to freezing by using no-time dough-making processes and reducing processing times. Today, specific yeasts are available which are more resistant to freezing and thawing and are therefore more suited to frozen dough production.

In refrigerated (retarded) dough, storage temperatures are not usually low enough to freeze

the dough. It is possible to use refrigerated temperatures a little below 0 °C because concentration of solutes in the dough, especially salt, depress its freezing point; this means that the yeast cells should not be susceptible to freezer damage and so should retain their viability throughout the storage period.

Formulation and production of frozen dough

Dough temperature

For the reasons discussed earlier, the production of dough for freezing needs to limit yeast activity prior to freezing. In practice this means that bulk fermentation of dough as a means of developing the gluten network has limited or no potential. Straight or no-time dough making processes, or sponge and dough where the final dough is given no "floortime" seem to be best suited to frozen dough production (Cauvain and Young 2006b; Cauvain 2007b). While some benefit in terms of reducing yeast activity prior to freezing may be gained by lowering the final dough temperature for frozen dough production, it is worth bearing in mind that a lower a dough temperature will also reduce the activity of added functional ingredients such as ascorbic acid, and this can itself lead to a loss of dough gas retention. Nevertheless, it has become common practice in manufacturing environments to use a lower final dough temperature the in dough preparation stages.

Flour and improvers

Flour protein levels may be raised in the manufacture of frozen dough products to improve the gas retention properties of the dough. This may be achieved through the use of higher protein wheats in the miller's grist or by the addition of dried, vital wheat gluten. Typically protein contents will be 13% or more (on a dry weight basis).

It is common practice in the manufacture of frozen dough to use some form of improver to aid dough gas retention. This practice is especially useful in that such additions can be used to combat some of the negative effects which arise from changes occurring in the dough during storage and from the negative effects of disrupted yeast cells. Often the practice is to increase the level of improver additions, either alone or in combination above that used for scratch production. Ingredients which make positive contributions to frozen dough quality include ascorbic acid (or other dough oxidizing agents) and emulsifiers. The former improves dough gas retention through improved dough oxidation and the latter by reducing gas bubble coalescence in proof and the early stages of baking. The addition of a high melting point fat has benefits for gas retention similar to those of emulsifiers (Williams and Pullen 2007).

While enzyme additions have many beneficial effects for scratch and par-baked bread production, their use in frozen dough may require more careful thought. One of the reasons for caution is that defrosting times for frozen dough pieces can last many hours and even though enzyme activity will be reduced at lower temperatures, some negative effects may be observed because of the relatively long processing times involved. Improvers may be specifically formulated with different combinations of enzymes for frozen dough production to deliver enhanced gas retention properties.

Yeast level

Defrosted frozen dough will take longer to reach a given proof height than scratch production, or be smaller in size at the end of a given proof time. In part this is because of the loss of yeast activity which results from the freeze–thaw processes and this means that in

practice it is usual to increase the level of yeast used in the initial dough formulation. Such actions can restore dough proof volumes ([Figure 30.2](#)) and times to similar levels as fresh dough (Cauvain 2007b), but increase the risk of excess yeast activity prior to freezing and the risk of greater impact from de-vitalized yeast cells when the dough is defrosted. The level of increase depends on the length of the frozen storage time and the strain of yeast which is being used. For frozen storage times of 1–2 weeks it may not be necessary for any increase, while for up to 3 months around 50% extra yeast may be required, and beyond 3 months it may be necessary to double the standard recipe yeast level. Yeast level increases with strains which are intended for frozen dough production will be somewhat lower than the quoted numbers.
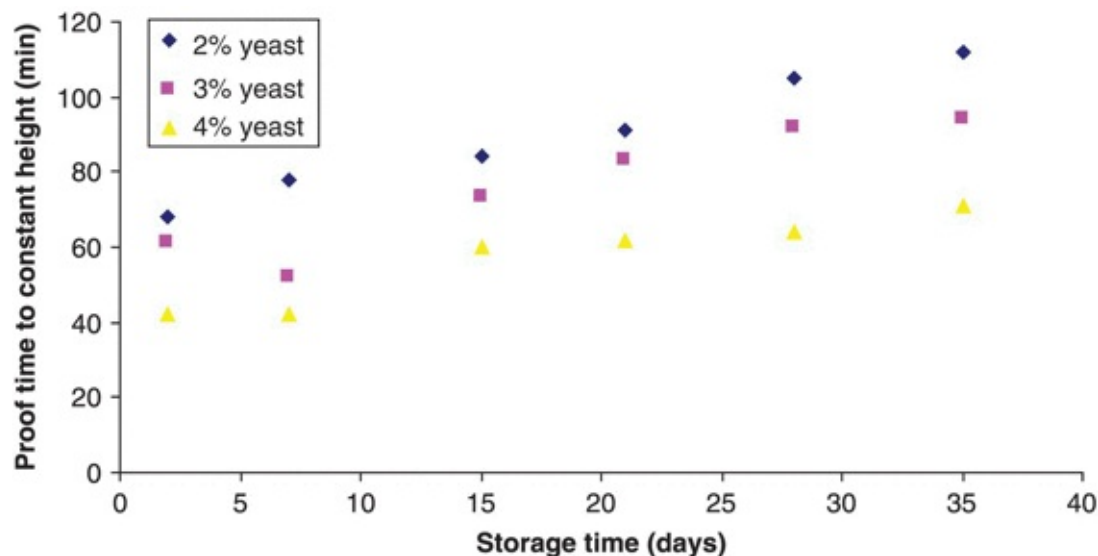
Figure 30.2 Effect of yeast level in frozen dough (stored at −20 °C) to constant proof height after defrosting.

Freezing and storage

Key determinants of the rate at which dough pieces will freeze are the temperature differential between the dough and the air in the freezer unit and the dimensions of the unit pieces. As noted earlier, the relatively poor conductivity of dough plays a significant role in determining how long the dough units remain in the freezer and what internal temperature they should achieve before they are transferred to the storage freezer. The impact of low temperatures on yeast cells and their subsequent activity are also important and it is commonly recommended that air temperatures below −35 °C are avoided (Cauvain 2007b). The limiting factor is the impact on the yeast cells which are significantly greater when the dough temperature is lower than −35 °C. In practice this means that liquid carbon dioxide and nitrogen tunnels have limited applications in the manufacture of frozen dough. Low freezing rates – such as those experienced when using a domestic-style freezer – should also be avoided to limit the potential for any gas production in the dough.

A common practice in the production of frozen dough is to leave the units in the freezer until they have achieved a core temperature of around −10 °C before transferring them to storage at −20 °C. This practice does not usually have any deleterious effects on the performance of the dough on defrosting, but holding dough units at higher storage temperatures may result in adverse dough quality changes, for example a lengthening of final proof times to reach the required dough height ([Figure 30.3](#)). Cauvain (2007b) provides graphs to show the rate at

which the core temperature of different weights and sizes of dough pieces freeze (core temperature −10 °C in a blast freezer with an air temperature of −30 °C); the times concerned ranged from 15 to 120 min for small rolls (60 g) to large pan dough units (910 g), respectively.
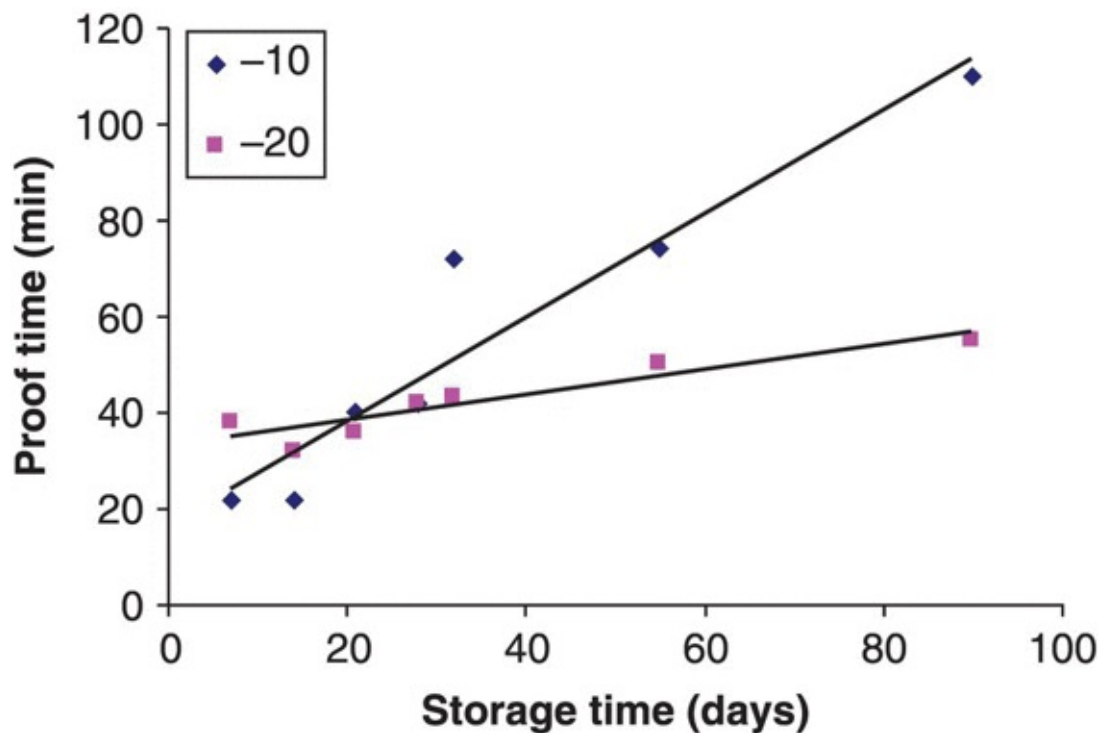
Figure 30.3 Effect of frozen storage temperature (°C) on dough piece final proof time to a given height.

Freezer damage and subsequent loss of product quality are exacerbated by fluctuations in freezer storage conditions, especially at temperatures close to the freezing point of the dough. Thus, once frozen, the temperature of dough pieces should be kept below −15 °C (Brummer 1995) and partial defrosting and refreezing should be avoided.

Defrosting and proving

To defrost and prove frozen dough pieces, the input of heat and humidity are required. Once again the relatively poor conductivity of dough plays a significant role and to optimize final product quality, the temperature differential between the surface and the centre of the dough piece entering the oven should be minimized. Cauvain (2007b) provides curves which show the progressive increase of the core temperature of different sized dough pieces when held at 21 °C. The time required to reach a core temperature of 5 °C (high enough to allow transfer to a prover) ranged from 30 to 180 min for rolls (60 g) and pan bread (910 g), respectively. Typically, defrosting would be followed by a period of proving which may add 30–120 min to the processing times required for the dough pieces to be ready for baking.

Pre-proved frozen dough

The long defrosting and proving times typically required for frozen dough units have led to interest in freezing fully or pre-proved dough pieces. The intention is for the dough pieces to be taken from the freezer and transferred to the oven with very short or no resting (recovery) time. Frozen dough units using this approach are available although the application the relevant technology does not cover the full range of fermented products which would be available from scratch or par-baking. The fermentation which occurs in proof increases the susceptibility of the yeast to freezer damage and in practice, it is likely that few, if any yeast cells survive the freezing and storage cycles in a viable condition. This limits the potential for the generation of any carbon dioxide gas post-frozen storage.

In proved dough, the gas bubbles are inflated by mostly a mixture of nitrogen and carbon dioxide, any oxygen which was entrained in the dough is usually scavenged by the yeast cells (Cauvain and Young 2008). At the warm temperatures experienced during proof, the carbon dioxide gas goes into solution in the dough liquor before diffusing into the nitrogen gas bubbles. When the dough is cooled the diffusion process is reversed because of the higher solubility of carbon dioxide at low temperatures compared with that of nitrogen. Without the carbon dioxide gas the nitrogen gas bubbles shrink and some of them diffuse out of the dough. During storage, the diffusion processes may manifest themselves as progressive collapse or shrinkage of the dough pieces. Since there is not likely to be any "new" carbon dioxide generated post-freezing, then dough expansion and final product quality may be severely affected unless the dough layers remain intact.

For the reasons outlined earlier, the use of pre-proved frozen dough is limited in terms of storage times and range of suitable products. Pre-proved frozen dough technology has been applied to one group of products, namely fermented laminated products such as croissant and Danish pastries. The reason for this successful application is that a significant part of the lift obtained with such products comes from the steam pressure generated during baking which forces the dough layers apart as they are heated (Cauvain and Young 2001). This lift mechanism means that there is less reliance on the generation of carbon dioxide in the post-freezer phase.

Formulation and productionof refrigerated dough

Dough making and processing

With refrigerated (retarded) dough, the storage temperatures are not usually low enough for the dough to freeze and the yeast cells should largely remain viable and active. This means that all the common methods employed for dough making may be used; however, best results are obtained when using no-time dough making processes.

As with frozen dough, there is sometimes a temptation to use lower than normal final dough temperatures in the production of refrigerated dough as a means of limiting yeast activity before cooling and storage. This should be avoided whenever possible as it can have adverse effects on final product quality, as discussed earlier.

Ingredients and formulation

Usually it is not necessary to change ingredients or formulation for the production of refrigerated dough. The maxim should be "if the ingredients and formulation make good standard bread with scratch production, they should make good products using the appropriate retarding conditions". The key is to choose the most appropriate refrigerated storage and proving conditions for the chosen products, and this is discussed later. Composite improver formulations are available for refrigerated dough production and these may be similar to those used for frozen dough.

The only ingredient change that might be required is to the level of yeast in the recipe. For refrigerated no-time dough, the change is commonly to reduce the yeast level to compensate for the continuing gas production during storage rather than to increase yeast levels to compensate for the loss of cell viability with freezing. The other benefit in reducing yeast level is that it can contribute to more uniform proof after storage as discussed later.
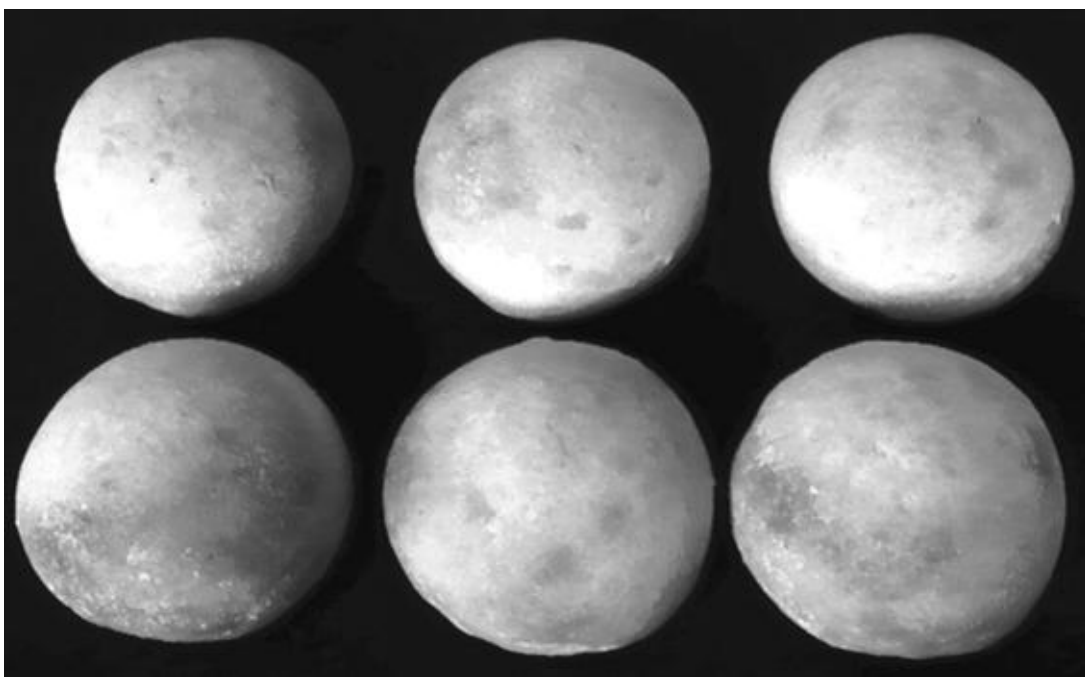
Refrigeration and storage

Refrigerated dough is typically stored at temperatures between −5 and 3 °C and better product quality is normally obtained by using as low a storage temperature as possible without freezing the dough pieces. As would be expected, small dough pieces cool more rapidly than large ones. This means that lower refrigeration and storage temperatures are more important with larger units in order to reduce the core temperature more rapidly and thereby limit gas production. If refrigerated dough pieces are cooled too slowly then there is a tendency for the formation of small white, almost translucent spots on the baked product surface (Figure 30.4) (Cauvain 2007b).

Figure 30.4 Formation of white spots (left) on retarded rolls, standard products right.

A particular problem with refrigerated dough is the potential for dehydration during storage, which causes a grey-white discoloration of the product surface (Figure 30.5) and gives the crust a rough, gritty feel. The design of the equipment is intended to reduce the risk of these problems but with storage potentially lasting several days, the risk of dehydration (known as skinning to bakers) is significant. In this context, storage temperature, time, and surface area of the dough piece are important. Lower temperatures tend to reduce the potential for dehydration especially with longer storage times. Cauvain (2007b) showed that weight loss (dehydration) was reduced if the recipe yeast level or the storage temperature (or both) were reduced because there was less expansion during storage and therefore less surface area from which moisture could be removed.

Figure 30.5 Retarded products showing the effects of skinning (surface dehydration).

Storage times for refrigerated (retarded) dough are commonly up to 72 h, depending on temperature and unit size. Longer storage periods are obtained with lower temperatures and small units are better suited to longer storage times.

Proving and baking

The warming and proving of refrigerated dough in preparation for baking may be carried out in conventional provers or automatically in a pre-programmed retarder-prover. Whatever the choice of equipment, a key requirement is to deliver the dough to the oven without major temperature differentials between the surface and the core. For small units such as rolls, this is relatively easy but with larger units longer times and lower proving temperatures are necessary. All refrigerated dough products benefit from using lower prover temperatures, typically in the range 20–32 °C. A longer proof time is required at these lower temperatures but when the dough is being held in an automatic retarder-prover, the timing of the change from cold to warm conditions matters little.

Usually there is no need to adjust baking conditions when using refrigerated dough. However, in some cases the extended storage period allows increased enzymic activity in the dough with a subsequent increase in the levels of residual sugars. These can take part in the Maillard browning reactions and may deliver an excessively dark crust color with some baked products. A slight reduction in baking temperature may help alleviate this problem or it may be necessary to use an improver system with lower enzymic activity.

The manufactureof par-baked products

Par-baked products present ready-to-use bakery products in a relatively convenient form. In essence, par baking forms the required product structure but does not "complete" the baking process, which in most cases means that the product needs to be re-heated to deliver the required product color, crust characteristics, and crumb softness. The technology was developed in 1949 reputedly by a Florida-based fireman whose roll baking expertise was interrupted by the fire alarm and he ended up re-baking incompletely baked products (www.forumsforums.com/3_9/archive/index.php/t-51814.html). The idea was taken up by companies such as General Mills and by the 1950s products being described as "Brown 'n Serve" reached the market place in the United States and the United Kingdom.

One advantage for par-baked products is that they can be held at ambient temperatures between manufacture and ultimate bake-off. However, one disadvantage is that the high water activity means that the product is susceptible to mold growth and they often have to be treated with preservatives or packed in a modified atmosphere, or both. Another way in which longer shelf-lives may be achieved is by refrigerating or freezing the par-baked product though such approaches reduce the immediacy of availability for bake-off associated with ambient stored products. In addition to microbial shelf-life limitations, the characteristics of par-baked products change during storage as the result of bread "staling". Re-heating the product at the point of bake-off should reverse the changes which are the result of staling, provided it is carried out in an appropriate manner, see discussion later.

Ingredients and formulations

Major changes to the choice of ingredients and formulations are not usually required for the successful production of par-baked products. Bread improvers for par-baked products are usually formulated with ingredients which will contribute to dough stability, especially towards the end of proof, so the inclusion of emulsifiers and enzymes such as lipase is common. Stear (1990) suggests a small reduction in yeast and yeast foods to avoid excessive oven spring, in part because of the lower baking temperatures which are employed for the first bake. A reduction in the level of water used in the dough formulation to preserve the shape of free-standing breads is sometimes recommended (Stear 1990). A common practice with stick-shaped products is to support them in nets or slings for processing through to cooling.

Proving and first bake

Par-baked and scratch-baked products differ in the processes of proving and baking. The aim in the manufacture of both types of products is to create the required structure, though for par-baking, crust color formation will be less; to achieve these twin objectives, some adjustments to processing times and temperatures need to be made. Brown (1993) considered two baking methods to achieve minimum crust formation and color; the first being based on a low temperature for the normal baking time. This requires a reduction in proof time (or a reduction of yeast level) to take account of the resultant increase in loaf volume caused by the delay in the dough piece "setting". The second option was to use a

higher temperature bake to set the dough structure quickly, followed by removal from the oven before the crust has set or colored. The choice will depend in part on the product diameter, with large diameter products being better suited to the first option. A less aerated, lower volume dough piece is found to favor the maintenance of the part-baked bread structure. Longer final proof times produce part-baked breads with higher volumes and lower stability. It is often recommended that the top surface cutting of dough pieces made from dough with less added water and shorter final proof times should be a little deeper.

Par-baked products tend to be rather delicate after baking and are prone to shrinkage on cooling which often leaves behind a wrinkled surface. Pyler (1988) considered that to avoid such shrinkage and collapse, the internal product temperature ex-oven should exceed 77 °C and preferably reach 82 °C, which would require products to be baked at between 120 and 150 °C for as long as possible without the formation of crust color. However, more recently the move has been to achieve product core temperatures approaching 90–92 °C to ensure greater par-baked product stability. The oven conditions required to achieve such higher core temperatures may lead to the formation of more crust color but this has become more acceptable for some markets, such as food service and catering.

Cooling and storage

Because of the relatively delicate nature of par-baked products when they leave the oven after first bake, methods have been sought to reduce shrinkage and collapse; one approach is to subject the par-baked units to vacuum cooling. This involves moving the hot units into a separate chamber after baking and reducing the atmospheric pressure. Whatever the method used for cooling par-baked products the core temperatures needs to be lowered to around 30 °C to avoid condensation in the pack which could encourage the growth of molds with products stored at ambient temperatures.

It is a common practice with par-baked product to include suitable anti-microbial agents in the dough formulation, especially if the products are to be held at ambient temperatures for any length of time. As an alternative, or sometimes in addition, the product surface may be sprayed with a solution of a suitable mold inhibitor, for example sorbic acid or potassium sorbate, before packing. The other main technology used for extending the mold-free shelf life of par-baked products is to use gas flushing. In this case the air from the pack is commonly replaced with a mixture of nitrogen and carbon dioxide (Pateras 2007). Gas flushing may be used instead of ant-microbial agents but may also be used in conjunction with them to deliver a significantly extended mold-free shelf-life.

Impact of re-heating (bake-off)

Bread staling is a term used to encompass various unwanted changes in the organoleptic qualities of bread products and there are several processes which contribute to staling. A key underlying reason for bread staling is the time and temperature-dependent retrogradation or recrystallization of the starch component of the wheat flour (Chinachoti 2003). The main physical manifestation of this retrogradation is the firming of the bread crumb. This firming starts as soon as the product leaves the oven and begins to cool. In the model proposed by Schoch and French (1947), in the first minutes of cooling it is the retrogradation of the amylose component of the wheat starch that is involved in this initial firming, while much of

the longer-term staling involves recrystallization of the amylopectin. It is the later changes that are most commonly referred to as staling. The maximum staling rate for bread is considered to take place at refrigerated temperatures.

It is well known that when stale bread is re-heated the crumb once again softens. In practice this means that par-baked breads are effectively refreshened at bake-off. However, after the second bake the rate at which subsequent staling takes place is greater than after the first bake. In this context the temperature achieved in the second bake becomes critical as is it important that all starch crystalline structures are melted. This is because any remaining crystals which have not been melted during the second bake act as seeds for the subsequent recrystallization process. In practice this means that the core temperature of par-baked products at bake-off should reach 65 °C (Cauvain and Young, 2009). A further factor in determining the final quality of par-baked products is their moisture content. Having undergone two baking stages, the final moisture content can be lower than would normally be achieved in scratch baking. As well as contributing to drier, firmer crumb eating quality, the lower moisture itself contributes to a faster rate of staling in the product after bake-off.

In addition to changes in the quality of the product crumb, there may be changes in the character of the product crust. Many of the products chosen for par-baking are expected to have a crispy crust when consumed and so careful control of bake-off conditions is critical to final product quality (Le-Bail 2012). Typical bake-off temperatures are quoted as being in the region 210–220 °C.

Frozen par-baked products

Freezing par-baked products avoids the risks associated with short microbial shelf-life and bread staling. However, there are risks and disadvantages associated with this approach. One disadvantage is that a period of defrosting is required before the products are transferred to the oven for bake-off. Care needs to be taken during this period to achieve thorough defrosting so that the product core temperature reaches the required target temperature at bake-off. Failure to do so will yield a firm bread crumb which rapidly stales. The process of freezing and defrosting of a par-baked or baked product is generally considered to be equivalent to 24 h storage under ambient conditions (Pence and Standridge 1995) because the product must pass twice through the temperature range over which bread staling is at its maximum.

Periods of partial defrosting and refreezing of the products should be avoided as this may lead to loss of quality through the formation of opaque, harsh-eating patches in the crumb. The phenomenon is commonly referred to as "freezer-burn" (Cauvain and Young, 2008) and is often found a few millimeters under the crust. If the first baking conditions are not optimized then the crust of frozen par-baked products may become detached, usually after the second baking (Cauvain and Young 2009) and, if combined with poorly controlled frozen storage conditions, may even occur in the freezer before products can be baked-off.

Conclusions

Refrigerated and frozen dough and par-baking technologies are all designed to enable the interruption of the scratch baking process and deliver units to a bake-off facility at some distance from the original bakery. Each of the technologies employed is intended to provide convenience and ease-of-use at the bake-off point. In many cases the products may supplement scratch production of other bread products. All of the technologies are relatively mature having been in use since the 1950s. Though new developments and applications continue to be introduced, the basic principles of the technologies remain the same as when they were first introduced.

Convenience is often cited as the reason for implementing these technologies yet, in the earlier discussions, various relatively "inconvenient" product changes have been identified. In addition, a number of practical problems in implementing these technologies have been highlighted showing that they are not always as easy-to-use as they are presented. In the production of all bakery products, careful choice of the appropriate raw materials and formulation must be coupled with appropriate and controlled processing methods. The technologies discussed in this chapter are no exception; indeed, with the introduction of extra processing steps it might be argued that greater control is needed than with scratch production.

None of the technologies outlined is likely to provide a product which is superior to scratch baking but this does not mean that they do not play an important role in the manufacture and availability of baked products.

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31
Steamed Bread

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Introduction and definitions

Chinese steamed bread is widely known as 'eastern bread' and has been consumed in its various forms for more than 1700 years. Although it originated in China, its popularity has spread to Japan, Korea, and Southeast Asia (Figure 31.1).

Figure 31.1 Steamed products in their various forms: steamed bread, buns and rolls.

Steamed bread is the staple food in the wheat growing areas of northern China. It may be consumed at all meals and is usually eaten hot. Dough for Chinese steamed bread is made from fermented wheat flour or blends of wheat and other grain flours. The product is cooked by steaming in a steamer. The most common types of steamed breads are either round or roughly cylindrical in shape with a white, smooth, shiny skin devoid of crust. Texture varies from dense to open and the flavor is dependent upon local tastes (Huang and Miskelly 1991).

Like European bread where one piece of bread dough can be used to make different forms of products such as pan bread, rolls, and buns, the same piece of steamed bread dough can be used to make different forms of steamed products such as steamed bread, steamed buns, and steamed twisted rolls (Huang 1999). Steamed products can be made with and without fillings.

Traditionally, steamed bread was made at home by hand. Today, in cities, almost all steamed bread, buns and rolls are made in small factories. These modern factories use mechanical mixing, sheeting, and even rounding. Therefore, in this section, all topics on steamed products refer to products made using mechanical processing.

Steamed bread

Steamed products without fillings are called steamed bread (mantou or moo). Typically steamed bread weighs about 65 or 130 g, and has either a round or cylindrical shape (Figure 31.2). A small-sized steamed bread, weighing only 25 g, is becoming very popular in Guangdong province.

Figure 31.2 Steamed bread.

Steamed buns

A steamed product with a filling is called a steamed bun. Steamed buns (bao zi or bao) are made with various delicious sweet or savory fillings (Figure 31.3).

Figure 31.3 Steamed buns.

Steamed rolls

Steamed rolls (huajuan or juan) are another popular form of steamed product. Particular condiments are spread between the layers of dough. The cutting, stretching, rolling, folding, and steaming processes produce numerous varieties of steamed rolls with different shapes and flavors (Figure 31.4).

Figure 31.4 Steamed rolls.

Steamed cake

Steamed cake (zhenggao or fagao) is usually made using wheat flour, rice flour or a blend of wheat and other grain flours. Steamed cake has a soft and fluffy texture and sweet taste. The texture of steamed cake is either very open and coarse with a flat shape (fagao), or very fine and similar to western cake when the ingredients include sugar and eggs (zhengzhi dangao).

Classification – three styles of steamed bread

Throughout Chinese history, various forms of steamed products such as steamed bread, buns, and twisted rolls have been developed. Because of the regional differences in geography, weather, agriculture products, and different eating habits, quality preferences and processing formulas were established for steamed bread ([Table 31.1](#)). In northern China, wheat is the main crop and people have steamed bread as their staple food. People in northern China prefer steamed bread with a firm, elastic, and cohesive eating quality to achieve a satisfied full stomach feeling for longer. In addition, the steamed bread needs to have good chewing properties and a natural wheat flavor. It was indicated (Anon 1989) that the well-known varieties of northern style steamed bread included: Gaozhuang mantou (in Shangdong province), Guan Guan Mo (in Shaanxi province), Gang Zi Mantou (in Kaifeng, Henan province). In southern China, however, rice is the staple food. People in the south often have steamed bread and rice porridge for breakfast. The southern style steamed breads preferred are soft and a bit chewy; the most popular variety is Xiao mian mantou (Anon 1989). In lower southern China – the Guangdong region – where the influences from the north and abroad are strong, people have rice as the staple food, but enjoy a wider choice of food. In the Guangdong region, unique steamed products have been developed according to local eating habits and preferences based on the two styles of steamed bread (Shuai 1998). Local people only have small steamed breads after meals as sweets, which is a result of western influences as Chinese people do not usually have dessert after a meal. A well-known variety of Guangdong style steamed bread is Naibai mantou (Shuai 1998).

Table 31.1 Classification of Chinese steamed products

			Quality characteristics			
Form	Style	Texture	SV[a]	SR[b]	Structure	Eating quality
Staple food						
Steamed	Northern	Very firm	2.0	1.2	Very dense	Very firm and cohesive
bread		Firm	2.5	1.5	Dense	firm and cohesive
	Southern	Soft	3.0	1.6	Open	Soft, a bit cohesive
Non-staple food						
	Guangdong		3.2–3.4	1.7	Open	Very soft, not cohesive
Fancy steamed bread						Varies – depends on variety
Steamed buns and rolls					Open	Soft and slightly cohesive
Guangdong buns					Open	Very soft, not cohesive
Char shiew bao					Open	Very soft, fluffy and not cohesive
Steamed cake					Open	Very soft, fluffy and low cohesiveness

[a] SV, Specific volume = volume/height.

[b] SR, Spread ratio = width/height.

There are three styles of steamed bread in China and in east and south-east Asia: northern, southern, and Guangdong styles (Huang and Quail 1996a). Here style means different ingredients and different quality characteristics. It should be emphasized that the three styles of steamed bread refers to steamed products without fillings. The differences in dough for steamed buns and rolls (products with fillings) consumed across China are much less than for steamed breads.

Su (2005) suggested classifying Chinese steamed bread into two categories: staple food and non-staple food. The steamed bread consumed as staple food was subdivided into three types based on firmness: soft, medium, and hard. He indicated that soft staple steamed bread was equivalent to the southern style suggested by Huang and Miskelly (1991), while both medium and hard steamed breads were equivalent to the northern style of Huang and Miskelly (1991).

Differences

Ingredients

The ingredients are very simple for northern and southern styles: flour, water, and yeast or sourdough (Huang and Miskelly 1991). For Guangdong style steamed bread, however, up to 25% sugar and 10% fats or oils are used (Huang and Quail 1997). Traditionally lard has been used extensively. Baking powder, particularly ammonium bicarbonate, has also been used to increase softness. Dried milk powder or fresh milk has often been used to enhance the flavor and protein content.

Key steamed bread quality parameters include specific volume, spread ratio, skin smoothness, color, and texture.

Specific volume

The specific volume (SV) of steamed bread is less than 2.5 for northern style, around 3.0 for southern style, and 3.2–3.4 for Guangdong style.

Texture and eating quality

There are obvious differences in the texture and eating quality among the three styles of steamed bread. Northern style steamed bread is characterized by its dense texture, firm, elastic, and very cohesive eating quality. The texture of southern and Guangdong styles is open. People in southern China prefer steamed bread which is soft and a bit chewy. Guangdong style steamed bread has a unique eating quality, which is very sweet, very soft and elastic, but not cohesive. People have this style of steamed bread after a savory course and they often dip it in very sweet condensed milk.

Geographically we can draw a picture of the quality preferences for steamed bread in China. From north down to the south, the preference for cohesiveness gradually reduces, while for softness and sweetness it gradually increases. When it is understood that people in different regions of China have different quality preferences for steamed bread, it helps to explain why people in Guangzhou do not like Gao Zhong mantou. Similarly people in the north do not enjoy the Guangdong style.

Popular areas

Northern-style steamed bread is popular in northern China. Steamed bread in Taiwan is a rather sweet version of northern-style steamed bread, which has a very cohesive texture (locals called "Q") and a slightly sweet taste. Southern style steamed bread used to be popular only in southern China, but now it is popular throughout China as a result of the use of the "no-time" fermentation procedure – after mixing dough is divided straight away, molded, then proofed, and steamed (see detailed section of dough preparation: one-step fermentation). Guangdong style steamed bread is not only popular in the lower part of southern China – Guangdong, Fujian, and Hainan provinces –, but also in the Hong Kong region and Singapore. Steamed products consumed in East and Southeast Asia are steamed buns (based on the dough formula for Guangdong style steamed bread). In Japan and Korea, steamed buns are most popular during winter.

Major ingredients for dough

Northern and southern style steamed bread is made from a simple formula: wheat flour, water, and yeast or sourdough. Guangdong style steamed bread also uses other ingredients such as sugar and fat. These ingredients are referred to here as the major ingredients and their roles in steamed bread are discussed. Flour from other grains and emulsifiers are referred to as optional ingredients and are discussed in a later section.

Flour quality

Wheat flour is the major ingredient of steamed bread. Its major components – protein, the water-soluble fraction, and starch – play a very important role in determining the quality of steamed bread (Faridi and Rubenthaler 1983; Lin 1983; Addo and others 1991; Rubenthaler and others 1992; Huang and Quail 1996a, 1996b, 2000). Finney (1978) pointed out that "a flour of good quality for bread baking should have high water absorption, a medium to medium–long mixing requirement, satisfactory mixing tolerance, good loaf volume potential (considering protein content), and should yield a loaf with good internal crumb grain and color." Tipples and others (1982) identify the "ideal" bread flour as one that produces good bread over a wide range of processing conditions, that yields dough with well-balanced handling properties, but that does not have long mixing requirements. The two elements of having good processing tolerance and making a good loaf of bread are also very important for steamed bread production.

Particle size

Zhou and others (1994) indicated that flour particle size had an effect on the quality of steamed bread. Flour particle size through a CB36 sieve (160 μ) is the most suitable for good steamed bread quality (Table 31.2). Flour that is too fine causes a decline in specific volume, flat steamed bread with a less attractive color, and more sticky eating quality, which results in a low total steamed bread quality score.

Table 31.2 Effect of flour particle size on the quality of steamed bread

Flour sample	Sieve size	Flour particle size (μm)	Flour whiteness (%)	Dough water absorption (%)	Steamed bread				
					Specific volume[a] (ml/g)	Spread ratio[b] score/15	Colour score/10	Non-sticky score/15	
1	54GG	≤318	73.3	60.5	2.33	14.5	8.5	13.5	9
2	CB30	≤181	75.0	61.9	2.25	14.5	9.1	13.1	9
3	CB36	≤160	76.9	63.2	2.2	14.5	8.3	13.0	8
4	CB42	≤123	76.8	62.9	2.19	10.0	7.5	12.0	8
5	CB54	≤105	79.2	67.2	2.11	10.0	6.6	10.8	7
6	150 mesh		83.4	74.2	1.92	9.0	6.9	10.6	7

[a] Specific volume = volume/weight.

[b] Spread ratio = width/height.

Color and extraction rate

White, shiny, smooth steamed bread with a bold shape are the most preferred features (Huang and Miskelly 1991). The color of steamed bread not only depends on the color of the flour, but also on the addition of alkali (for neutralization of the dough after fermentation), processing procedures such as sheeting (Huang and Hao 1994), and steaming rate (Chen 2007). A yellowish color is not acceptable to customers. Flour extraction rate is usually controlled to 60–70%. The steamed breads served in banquets utilize flour with an even lower extraction rate. The practice of bleaching flour is not liked by consumers, however, even though the steamed bread is extremely white.

Water absorption

The water absorption of flour used for steamed bread varies and depends on the style of steamed bread being made: for northern style it is around 60–63% (Huang and Quail 1996b); for southern style it is about 58–60% (Huang and Quail 1996a); and for Guangdong style it is about 58–63% when fat is included in the formula, and 54–57% when there is no fat in the formula (Huang and Quail 2003). For Char siew bao (Hong Kong style steamed buns with a Chinese barbecue pork filling), water absorption is about 50% (Limley 2008).
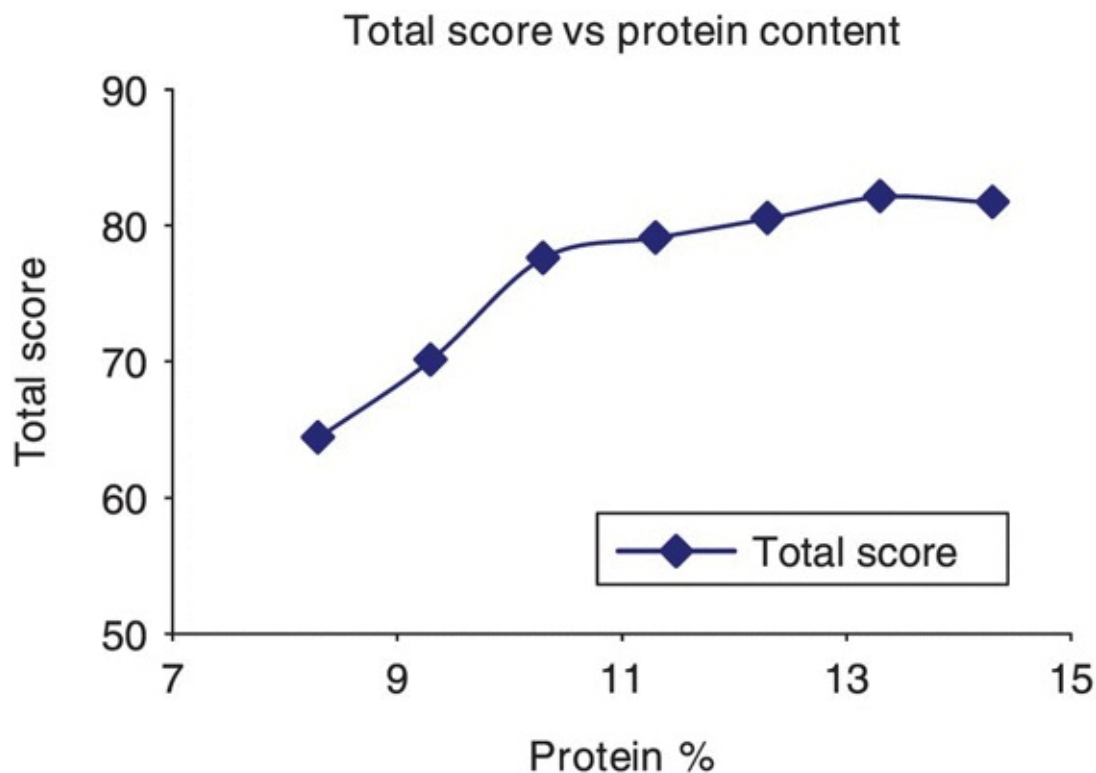
Protein content and quality

The relationship between protein content and steamed bread quality is not as clear as it is for pan bread (Addo and others 1991; Rubenthaler and others 1992). The first reason is the different nature of the two breads – steamed bread is steamed and has a soft and moist skin, while pan bread is baked in an oven, which forms a firm crust to support the loaf. The second reason is the different flour quality requirements for the three styles of steamed bread. The third is that steamed bread is more sensitive to the variations in processing conditions than pan bread; for example, the occurrence of wrinkles, brown spots, dimples, or even product collapse.

Using 43 Australian wheat samples and 6 samples of Chinese wheat, Huang and Quail (1996b) investigated the relationship between flour quality and the quality of northern style steamed bread. There was a significant linear correlation between the protein content and the specific volume and spread ratio of steamed bread. But there was no significant linear correlation between protein content and the total quality score of northern style steamed bread. However, when the flour protein content was below 10%, it was linearly and positively correlated with the total quality score of steamed bread. As protein content further increased, the total quality score was not significantly influenced by protein content and was more dependent on other flour quality attributes. This trend was very similar to that revealed by Faridi and Rubenthaler (1983). Overall, it was apparent that dough strength was more important than protein content in determining the quality of steamed bread.

By adding starch and gluten to a base flour, Huang and Quail (1999a) investigated the effect of flour protein content on the quality of Guangdong style steamed bread.

It was shown (Figure 31.5) that when the protein content was increased from 7.8 to 10.8%, the total quality score of steamed bread increased sharply and linearly. As protein content increased further, however, the total steamed bread quality score continued to increase, but at a much lower rate. This was consistent with the results mentioned earlier.

Figure 31.5 Relationship between the total quality score of Guangdong style steamed bread and protein content of reconstituted flour.

Using a fractionation and reconstitution technique, Lin (1983) and Huang and Quail (1999a) investigated the effect of flour components on steamed bread quality. It was shown that gluten was the most important determinant of quality of steamed bread; this was followed by the water-soluble fraction and then the starch fraction. The results also indicated a possible interaction between starch and water-soluble components.

It was also shown that high molecular weight glutenin (HMW) subunit 5 + 10 was related with a higher total quality score of steamed bread than the glutenin subunit 2 + 12 (Lukow

and others 1990; Wang and Li H 1998; Huang and others 2000; Zhu and others 2001; Zhang 2003).

The percentage of unextractable polymeric protein to total polymeric protein was positively and significantly correlated with the total quality score of Guangdong style steamed bread (Huang and others 2000). This result suggested that Guangdong style steamed bread required flour with good dough strength when fat is included in the formula. Zhang (2003) suggested that in a steamed bread wheat breeding program, it would be advisable to increase wheat protein content by increasing the total polymeric protein that contains a moderately higher proportion of unextractable polymeric protein, but its amount should not be as high as that in wheat intended for pan bread.

Starch

Starch was the least important fraction influencing the quality of steamed bread in comparison to the gluten and water-soluble fractions of flour (Lin 1983; Huang and Quail 1999a). Fan (1985) pointed out that steamed bread made from flour with high amylose content had poor eating quality, smaller volume, and low cohesiveness and sticky texture. Steamed bread made from flour with low amylose content had better eating quality, bigger volume, and a more cohesive and non-sticky texture. Huang and Quail (1996b) indicated that rapid viscoanalyzer (RVA) viscosity parameters were significantly correlated with northern style steamed bread quality.

At starch damage values less than 50%, a significant positive linear correlation ($\alpha = 0.01$) was found between damaged starch content and steamed bread quality scores (Zhou and others 1994). At a starch damage value of 50% or more, however, the steamed bread quality scores decreased. This negative linear correlation was highly significant ($\alpha = 0.01$). Furthermore, an increase in damaged starch levels caused a decrease in bread volumes. Flour with damaged starch levels within the range 20–50% produced satisfactory steamed breads (Zhou and others 1994; Shelton and Guo 1999).

Water-soluble components

The water-soluble fraction of flour is important to the quality of steamed bread (Lin 1983; Huang and Quail 1999a). The water-soluble fraction of flour (approximately 2–3% of total flour weight) contains albumins and globulins as well as water-soluble pentosans. According to Neukom and others (1967), wheat flour contains about 2–3% pentosans, of which about 20–25% are water soluble. The water-soluble pentosans are most frequently conjugated with proteins and possibly other polymers (D'Appolonia and Kim 1976). Huang and Quail's work (1999a) showed that there was varietal difference in the water-soluble fraction of flour. Interchanging the water-soluble fractions from two flours (Leichardt (A) – a strong hard wheat, and Albany (B) – a weak soft wheat) caused a decline in the total quality score of steamed bread made from the reconstituted flour with starch and gluten fractions from flour A and the water-soluble fraction from flour B, but increased the specific volume and total quality score of steamed bread made from the reconstituted flour with starch and gluten fractions from flour B and water-soluble fraction from flour A (Table 31.3).

Table 31.3 Quality differences between steamed breads made from original flours and reconstituted flours, and between steamed breads made from reconstituted flours, in which the water-soluble fractions were interchanged

Starch	Gluten	Water soluble	Specific volume	Total quality score (%)
Flour				
Leichardt (A)[a]			2.74	80.5
Albany (B)[b]			2.39	57.9
Difference			−0.35	−22.6
Reconstituted flour				
reconstituted components from:				
Starch	**Gluten**	**Water soluble**		
Leichardt[c]	Leichardt	Leichardt	2.56	79.2
Albany[d]	Albany	Albany	2.31	57.4
Difference			−0.25	−21.8
Leichardt[e]	Leichardt	Albany	2.63	78.7
Albany[e]	Albany	Leichardt	2.36	62.6
Difference			−0.27	−16.1

[a] a Control flour Leichardt (A).

[b] Control flour Albany (B).

[c] Reconstituted flour of Leichardt.

[d] Reconstituted flour of Albany.

[e] Reconstituted flour with interchanged water-soluble fractions.

Flour quality requirements for chinese steamed bread

Northern style

Using an optimized laboratory processing procedure (Huang and others 1993) and evaluation system for northern style steamed bread (Huang and others 1995), an investigation was carried out on 43 Australian and 6 Chinese wheat flours. As mentioned earlier, there was no significant correlation between protein content and total quality score of steamed bread, but a significantly high correlation between Extensograph maximum resistance and total quality score (see Figure 31.6, $r = 0.70$, $p < 0.001$). Huang and others (1996b) concluded that hard wheat flour was superior to soft wheat in the production of good-quality steamed bread. Flour with medium protein content, and medium to strong dough strength was recommended for the production of this product.
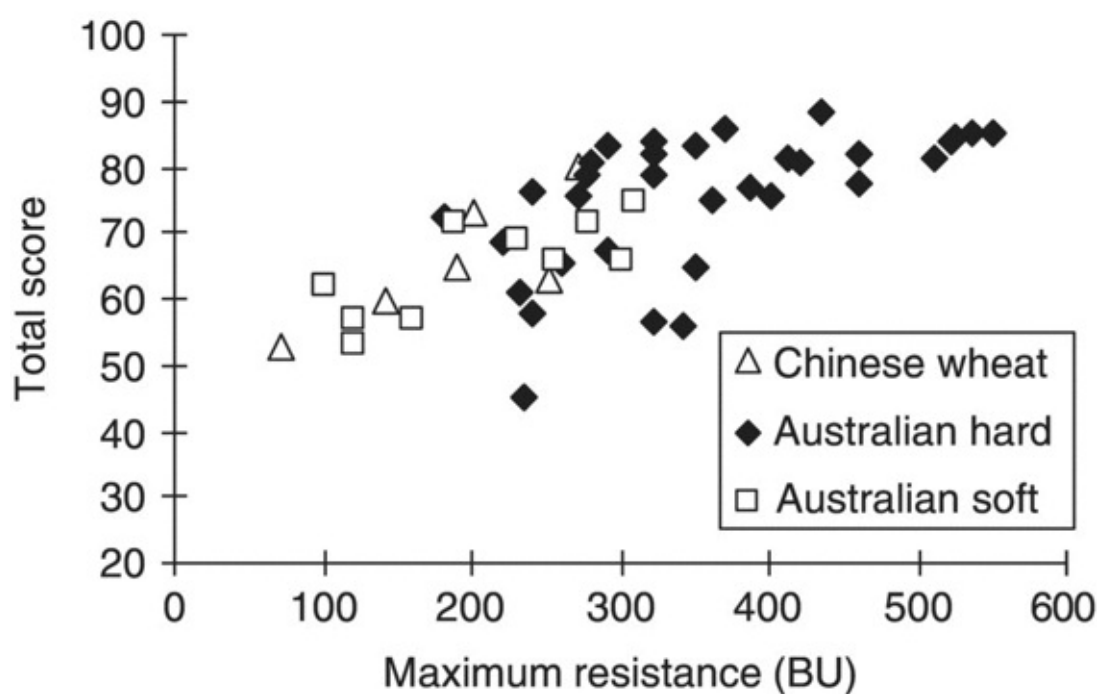
Figure 31.6 Total quality score against maximum resistance. $r = 0.70$, $p < 0.001$. (Ang et al. 1999. Reproduced with permission of Taylor & Francis).

Zhu and others (1997) further investigated northern style Chinese steamed bread and pointed out that flour protein content and dough strength were the main determinants of the quality of this style of steamed bread. Medium to strong flours with high protein content were best suited for northern style steamed bread production, but very strong flour was not desirable. Zhu and others (2001) found a significant negative correlation between Farinograph stability and steamed bread quality in Australian wheat, while a significant and positive correlation existed in Chinese wheat. This indicated that the Australian wheat used in that work was too strong, which was detrimental to the quality of northern style steamed bread.

Steamed bread consumed in Taiwan has characteristics that are close to northern style steamed bread, so it is very elastic and has a cohesive eating quality. Chen (2007) demonstrated that very good quality Taiwan type steamed bread can be made using flour milled from hard wheat and with higher than medium dough strength if it is combined with a higher than medium steaming rate. Zhang (2003) indicated that unlike pan bread, flours with a medium dough development time and slightly longer dough stability were most desirable for northern style steamed bread. Extremely strong dough strength should be avoided to prevent post-steaming shrinkage and the formation of surface blisters and wrinkles. Su (2005) found that flour with a medium protein content (10.5–12.5%) should be used for a medium-firm type of steamed bread (equivalent to northern style) and that the hard-firm type of steamed bread (also equivalent to northern style) needs flour with a medium to high protein content (10.7–13.5%).

It is advisable to have a good balance between flour protein content and dough strength, avoiding high values in both, particularly avoiding flours with excessive protein content and dough strength. For avoiding shrinking or collapse in the production of northern style steamed bread, it is advisable not to use aged flours because dough strength increases with increased storage time.

Southern style

Lin and others (1990) indicated that flour color and protein content seemed to be more important than other physical and chemical properties in determining the quality of steamed bread. Flour samples with a high protein content (> 12%) and strong dough produced bread with a wrinkled surface and dark color, whereas low protein (< 10%) soft wheat flours gave poor texture and eating quality, although the surface was smooth. It is suggested that flours of medium protein content (10–12%) and medium dough strength are the most suitable for southern style steamed bread.

Addo and others (1991) made 29 hard wheat flours (protein content 9.3–14.4%) and 34 soft wheat flours (6.7–15.5% protein content) into pan and steamed bread. They found that protein content was important in the production of acceptable steamed bread (especially from low-protein soft wheat flours). High flour strength was desirable in the production of pan bread (especially from high-protein hard wheat flour) and detrimental in the production of steamed bread.

Rubenthaler and others (1992) also found a negative correlation ($r = -0.76$) between protein content and steamed bread volume among hard red spring wheats, whereas the volume of steamed breads made from soft white, soft red, and club wheat flours were positively correlated with protein content ($r = 0.78$, 0.86 and 0.60, respectively). They concluded that flours that contain about 10–11% protein and were of medium to low strength are best suited for steamed bread.

An optimized laboratory processing procedure and evaluation system for southern style steamed bread were used to investigate the flour quality requirements for southern style steamed bread made from 50 Australian and 7 Chinese wheat flours (Huang and Quail 1996a). Again, both protein quantity and quality were identified as major determinants for the specific volume of steamed bread. There is no significant correlation between protein content and total quality score of southern style steamed bread. Protein content has a more significant effect on the specific volume of this style of steamed bread ($r = 0.67$, $p < 0.001$) than for northern style steamed bread($r = 0.49$, $p < 0.001$). Dough strength plays an important role in determining the overall quality score of steamed bread ([Figure 31.7](#)), but to a lesser extent than for northern style steamed bread. There was a significant negative correlation between external smoothness of steamed bread and protein content and between skin smoothness and flour dough strength. These results were consistent with that of Faridi and Rubenthaler (1983), Lin and others (1990), Addo and others (1991) and Rubenthaler and others (1992).
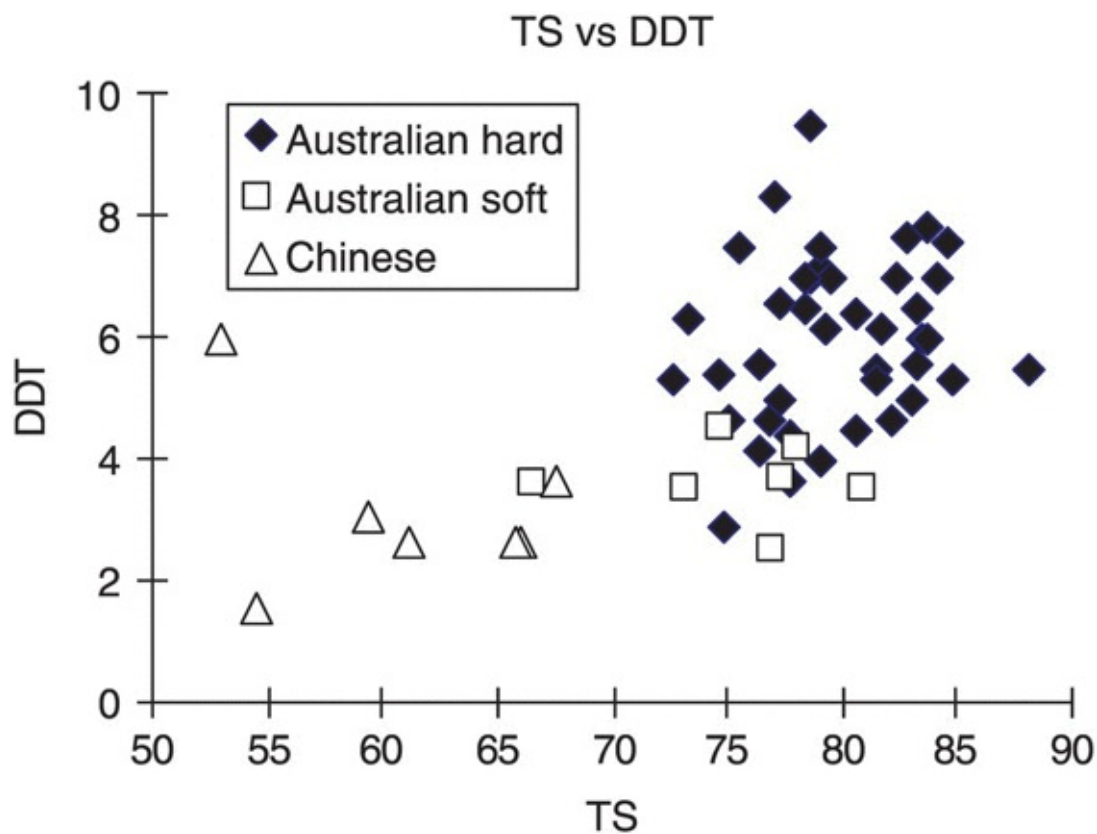
Figure 31.7 Total quality score (TS) against dough development time (DDT) for steamed breads made from 57 different flours. $r = 0.52$, $p < 0.001$. (Ang et al. 1999. Reproduced with permission of Taylor & Francis).

No single test can clearly define the flour quality requirement for southern style steamed bread. Hard wheat was found to be superior to soft wheat for this product. Flour with medium protein content and dough strength, a medium to high falling number, and low ash content were recommended for this product. No significant correlation was found between flour RVA viscosity parameters and the quality of southern style steamed bread.

Guangdong style

Guangdong style steamed bread is more sophisticated than the northern and southern styles of steamed bread. There are more ingredients used in different combinations than the other two styles of steamed bread. Guangdong style steamed bread has evolved from a staple food into a popular snack or dessert. The quality of flour used for this style varies appreciably. Sugar is usually used at a high level, but fat is not always included. Fat and sugar have a significant effect on the quality of Guangdong style steamed bread (Huang and Quail 1997).

To clarify the confusion of a large variation in flour quality being used for this style steamed bread, a consumer test was carried out in Guangzhou over 3 days (Huang and Quail 2003). Three flours: Albany (soft biscuit flour), Magnolia (local steamed bread flour), and D8062 (an Australian hard wheat flour) were used to make Guangdong style steamed bread using two formulas; with fat (A) and without fat (B). Table 31.4 shows the analytical data of three flours used in this consumer test.

Table 31.4 Flour data

Flour	Protein (%)	Starch damage (%)	Farinograph Water absorption (%)	Extensograph Development time (min)	Maximum resistance (BU)	Extensibility (cm)
Albany	8.1	4.2	52.3	1.8	150	17.2
White magnolia	8.9	6.4	54.2	1.2	342	14.2
D8062	11.1	8.7	63.9	7.7	490	20.4

The results of the consumer test on the eating quality of Guangdong style steamed bread are presented in Table 31.5. There were significant differences in scores of eating quality among the four steamed breads made from three flours using formula A and B. The eating quality of the steamed bread made from D8062 using formula A was significantly higher than the other three steamed breads, while the eating quality of steamed bread made from Albany flour using formula B had the lowest score. The eating quality of steamed bread made from the 'white magnolia' using formula A was significantly lower than that of the steamed bread made from D8062 using formula A, but higher than that of steamed bread made from the same flour using formula B, though it was not statistically significant.

Table 31.5 Results of consumer test on the eating quality of Guangdong style steamed bread

Flour	Formula[a]	Score[b]	Preferred rate (%)
Albany	B	3.6[c]	4
White magnolia	A	5.4[d]	22
White magnolia	B	5.1[d]	19
D8062	A	6.0[e]	54

[a] Formula A: 20% sugar, 4% fat; Formula B: 20% sugar, no fat.

[b] Average scores of 90 measurements.

[c,d,e] Significantly different at $p < 0.01$.

These results clearly show that if fat was included in the formula, steamed bread made from medium protein content with medium to high dough strength were preferred by consumers in Guangdong. It was also shown that Guangdong style steamed bread needs flour with medium dough strength (such as White Magnolia) even when there was no fat in the formula. This trend occurred even though the protein content of the White Magnolia flour was only 8.9%. Weak dough strength was not desirable. Shuai (1998) also found that flour with medium dough strength is required for Guangdong style steamed bread and buns.

Char shiew bao – guangdong style barbecue pork buns

Guangdong style barbecue pork filled buns (char siew bao, also called Hong Kong bao) have a soft and fluffy texture and sweet taste. However, their flour quality requirements are very

different from the other steamed bread and buns. Limley (2008) made a systematic study of char siew bao and pointed out that soft wheat flours with 7.5–8.0 % protein content, weak strength, moderate to high extensibility, and low flour swelling volume were ideal for their manufacture.

Rain damaged (sprouted) wheat

Rain damage of wheat is a common phenomenon around the world. When mature wheat is wet, it begins to germinate. The presence of moisture releases enzymes to break down starch (amylases), protein (proteases), and oil (lipases). The enzyme with the greatest effect on wheat and flour quality is α-amylase. Weather damaged wheat makes poor quality pan bread, noodles, and steamed bread (Figure 31.8). A falling number test is a quantitative way to assess the amount of α-amylase present in wheat. Zhou and others (1994) found that steamed bread made from flour with a falling number below 200 s had small volume, poor appearance (flat shape and blisters on the surface), rough texture, and sticky eating quality. Steamed bread quality will be normal if the falling number is above 250 s.

Figure 31.8 Steamed bread made from sound vs. weather damaged wheat.

Water

Water is essential for the formation of dough, and has an important role in some of the major changes that take place during the production of steamed bread. The high moisture content of steamed bread is essential to its character, contributing to its softness, flexibility, and texture. Dough consistency can be controlled through water addition. It can determine the processability of the dough and affect the quality of steamed bread. Water temperature is also a major determinant of final dough temperature.

Water quality

The quality considerations applicable to water as an ingredient of steamed bread are similar to those of drinking water. Water should not contain harmful bacteria and should be free from objectionable odor, flavor, and color.

Hardness

The hardness of water is attributable almost totally to the presence of calcium and magnesium ions. Water of medium hardness, up to about 150 ppm as $CaCO_3$ is desirable for

steamed bread production as some mineral salts have a strengthening effect on the gluten. Excessive hard water is undesirable because it retards fermentation by tightening the gluten structure. Soft water is not good either as it tends to yield soft, sticky dough.

pH

High pH water is undesirable because it has a detrimental effect upon fermentation. Water with a pH value of around 6.5 resulted in the fermented dough achieving optimal pH and was the most suitable for steamed bread production (Liu 2005).

Yeast

Bakers' yeast has replaced the use of sourdough or "starters" for fermentation in most fully or semi-automated steamed bread factories. Rates of fermentation are higher and more consistent with bakers' yeast. Yeast fermentation is the process where sugars are converted into carbon dioxide, water, ethanol, energy, and a range of by-products. Natural sugar in flour, together with added sugar and maltose resulting from the breakdown of starch provide the substrates for yeast to ferment. The resulting carbon dioxide helps to create the crumb cell structure of steamed bread.

Variety

There are three types of yeast used in the manufacture of steamed products in China: compressed (fresh) yeast, active dry yeast, and instant active dry yeast. Instant active dry yeast is the most widely used because it is convenient to use, has a high rate of fermentation, and very high and stable fermentative activity without cool storage. However it is the most expensive type of yeast.

Use of yeast

Instant active dry yeast does not need to be activated before use. Rehydration of the active dry yeast is best carried out by suspending the yeast in ten times its weight of water at 40–45 °C. For compressed fresh yeast, suspension in five times its weight of water at 30 °C is recommended. For both types of these yeasts, the suspension is stirred for 10–20 min before use. It is important to maintain favorable conditions for yeast to grow throughout the process of steamed bread production. Yeast is very sensitive to temperature change and of course the fermentation rate changes with the change of temperature. The mixing process can cause big changes in temperature, particularly if the room and mixer temperature are not controlled. Water is often used to control the dough temperature. In spring and autumn, water of 30–40 °C is often used to suspend the yeast; in winter, hot water –not exceeding 45 °C – is used. In summer, cool water and sometimes even iced water, is used to mix the dough. Yeast is dispersed into the flour the first, water is then added to avoid direct contact of the yeast with water that is too hot or cold. On very hot days in summer, yeast is added during the last 5–6 min of mixing. It is also advisable to avoid direct contact of yeast with salt, sugar, or alkali.

Sourdough

In China, instant active dry yeast is widely used in steamed bread factories. However, starter or soughdough left from the previous day has also been used for the production of steamed

bread in some workshops and homes. When sourdough fermentation is used, the *Lactobacillus* spp. by-products make the fermented dough very sour (pH 3.7–4.0). The dough needs to be neutralized by adding alkali solution (such as 40% Na_2CO_3). It is critical to control this stage to produce good-quality steamed bread. If the dough is over-neutralized, the steamed bread will become yellow with a strong alkaline flavor and an objectionable, bitter taste caused by the hydrolysis of protein into small peptides. Steamed bread made from under-neutralized dough has a sour smell and taste, smaller volume, poor appearance, and dense structure. The pH of dough will be between 6.4 and 6.7 if the dough has been properly neutralized (Huang and Miskelly 1991). The addition of alkali assists fermentation as it neutralizes acids produced by lactic acid bacteria during fermentation and allows production of carbon dioxide and water by yeast. However, it does destroy some vitamins in the dough. The amount of alkali required varies with the extent of fermentation, temperature, and ambient conditions. Experience is required both in judging the correct level of alkali and in the technique of alkali addition. A kneading technique by hand, or the combination of mixing and sheeting by machine, can be used to achieve this goal (Mao and Xu 1999).

Traditionally, several sensory methods can be used to check the degree of neutralization. These include the smell, taste, and observation of structure of a cut dough section; the sound made when striking the dough with the palm of the hand; or cooking a test piece of dough (Anon 1989). The neutralization point can also be determined by checking the pH of the dough. When neutralization is complete, the dough may require further mixing, depending on the strength of the flour used and the style of steamed bread made.

Optional ingredients for dough

Wheat flour, water, and yeast or sourdough starter are regarded as essential ingredients for steamed bread. Other optional ingredients may be added to assist dough processing or to enrich steamed bread quality. In this section, ingredients used widely in steamed bread making are introduced briefly and their applicability to steamed bread production is discussed.

Flours from other grains

For health reasons, steamed bread has been produced using blends of wheat and other flours. These flours include maize, millet, sorghum, sweet potato, buck wheat, oat, and black rice. Up to 30% of maize (or millet, or sorghum, or buck wheat) flour was mixed with wheat flour (70%), sugar (4%), dry yeast (0.2%), and water (40%) to make steamed bread (Liu 2005). Steamed bread made from a mixture of wheat flour and other grain flours are smaller, darker, and denser.

Sugar

Sugar can be used to aid extended fermentation in flour which has a low maltose figure. Sugar levels of 8–10% effectively improved specific volume and the total quality score of steamed bread, but above 10% were detrimental to the quality of steamed bread, as shown in Figure 31.9 (Huang and Quail 1997). Kruger and others (1992) claimed that negligible changes in external or internal appearance, volume, width to height ratio or texture were observed when 0.5, 1.5 and 3.0% sugar were incorporated in the standard formulation for the control flour.
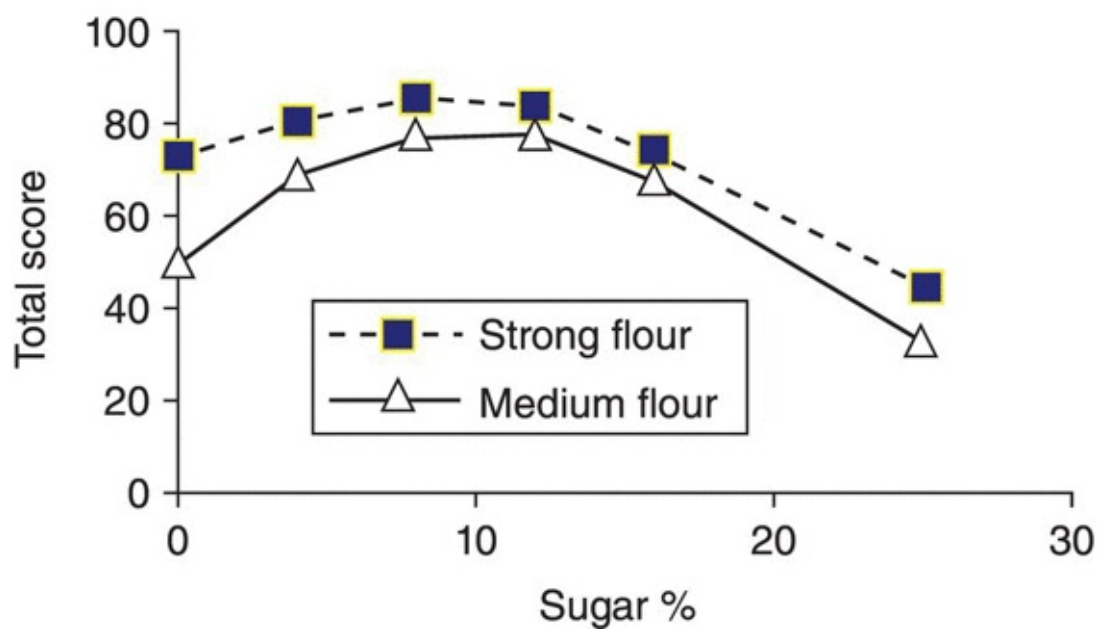
Figure 31.9 Effect of sugar level on the total quality score of steamed bread.

Fat and edible oils

Fat has a significant effect on the softness of steamed bread. Huang and Quail (1997) found

that for strong flour, up to 8% fat significantly increased the softness of steamed bread. Over that amount, softness was significantly reduced. For medium flour, up to 2% fat significantly softened the crumb of steamed bread. The total quality score of steamed bread was significantly increased up to 4% fat addition for strong flour.

The optimal level of fat addition to Guangdong style steamed bread was 2–4% (Huang and Quail 1997). Too much fat was detrimental to most quality attributes of Guangdong style steamed bread. Pomeranz and others (1991) pointed out that 2% shortening produced the best steamed bread: replacing shortening by soybean or corn oil produced comparable bread. Li and Cheng (1999) studied the effect of lard on the quality of steamed bread. They found that addition of lard improved the volume and color of steamed bread, softened the texture, and increased the eating quality. Lard also prolonged the shelf-life of steamed bread.

Alkali

Edible alkali such as Na_2CO_3 is often used in the processing of steamed products. Its function has already been described in the section of sourdough. Alkali can also be used to add some heavy metal to lower the hardness of water and weaken the interaction between the heavy metal and polar group in the dough, preventing the detrimental effect on dough and improving the color of steamed bread (Liu 2005).

Baking powder

Baking powder is used only for Guangdong style steamed buns. Baking powder improved the skin color and total quality score of steamed bread at a low dosage, but over 1% it seemed to have a detrimental effect (Huang and Quail 1997). Baking powder addition above 1% resulted in bitter flavors. A double acting baking powder is used for char siew bao to ensure a continuous supply of carbon dioxide during steaming to aerate the products.

Ammonium bicarbonate and/or a solution of potassium carbonate (known as lye water or *kan sui*) are alkalis commonly used to neutralize the sourdough so that the end product has a neutral taste. Ammonium bicarbonate also helps with dough aeration during cooking as it decomposes and release carbon dioxide gas when the dough temperature reached 40 °C.

Soy flour

The principal reason for the use of soy flour in the production of steamed products is its high biological value in terms of digestibility and amino acid composition. The key to the effectiveness of soy protein as a nutritional supplement is its high lysine content as compared to cereal proteins. Chruickshank (1996) found that the addition of soy flour (full fat) significantly improved the total quality score of steamed bread. The best improvement in total quality score was achieved by the addition of 0.6% soy flour. Higher levels of soy flour not only reduced specific volume and total quality score, but also imparted a noticeable soy aroma and flavor to the steamed bread. Lin (1983) carried out a sensory evaluation of steamed bread samples produced using 7.5% full-fat and defatted soy composite flour and reported that their acceptability was significantly less than the control.

The skin and crumb color of steamed bread can be significantly improved by the addition of up to 0.6% soy flour. The beneficial effect on the skin and crumb color may be attributed to

the bleaching effect that soy flour exerts on wheat flour dough. Soy flour interacts with the carotenoid pigments that cause some yellow-orange coloring in the flour. In pan bread, soy flour is often added at low levels to affect this bleaching action in white bread. Zheng and others (2006) reported that up to 2% addition of defatted soy flour improved the quality parameters such as color and specific volume of steamed bread.

Emulsifiers

Emulsifiers are active surfactant compounds that are widely used in bakeries as dough strengtheners and antistaling and crumb softeners. Wang and Wang (2006) studied the effect of the emulsifiers diacetyl tartaric acid ester of mono- and diglycerides (DATEM), sodium stearoyl lactylate (SSL), and calcium stearoyl lactylate (CSL) on the quality of steamed bread. They found there was a positive effect on the quality of steamed bread if the emulsifiers were used alone. However, the effect became obvious when the emulsifiers were used in combination. With 3 g/kg DATEM, 1 g/kg CSL-SSL and 8 mg/kg lipase, the color and structure of steamed bread improved markedly.

Enzymes

Enzymes are biological catalysts consisting primarily of protein. Bao and Wan (2008) reported that the addition of fungal α-amylase improved the appearance of steamed bread. The improvement in color of both the skin and crumb was maximized when 50 mg/kg fungal α-amylase was added. The specific volume of steamed bread was best at 30 mg/kg α-amylase addition, while the spread ratio was the lowest at this concentration of α-amylase. When all quality parameters were considered, the optimal addition of α-amylase was 30 mg/kg.

Lin and others (2010) reported on the effect of cellulase on the characteristics of dough rheology and the quality of steamed bread. They found that there was an increase in Farinograph water absorption, dough development time, stability and tolerance index when cellulase was used. The area of Extensograph curve and maximum resistance was increased and extensibility was decreased when the amount of cellulose addition was increased. The best improvement in steamed bread quality was achieved when 0.5% cellulose was used.

Hu and others (2003) studied the effect of lipase and a combination of lipase and CSL-SSL on the quality of steamed bread. The results showed that the improvement in color, external appearance, and eating quality of steamed bread reached the maximum when 15 mg/kg lipase was included in the formulation, but the specific volume was low. The combination use of lipase (25 mg/kg) and CSL-SSL (0.05%) achieved the maximum improvement in steamed bread quality.

Su (2005) studied the effect of xylanase on the quality of flour and steamed bread in both solid and liquid forms. It was found that the addition of xylanase in both forms decreased water absorption, dough development time, stability, and some other Farinograph parameters. The addition of xylanases also influences Mixograph parameters including decreasing the time to peak height. It was apparent that the softening effect of xylanase in both forms on dough accumulated with fermentation time. By including xylanase, fermentation time could be reduced by about 30% for southern style steamed bread. Inclusion of xylanase increased specific volume, spread ratio, and softness of steamed bread, but elasticity was unchanged. A trend of decreasing L^* and slight increase of a^* and b^* values

of Minolta color was also observed in the dough with the addition of xylanase in both forms.

A combination addition to the dough mix of 3 mg/kg amylase, 10 mg/kg xylanase, 4 mg/kg lipase, 18 mg/kg Vitamin C, and 5 mg/kg glucose oxidase has been reported to achieve the best improvement on the quality of steamed bread (Ren and Cheng 2007).

Salt

Salt has a conditioning effect on the dough. It acts to strengthen the gluten and to reduce the stickiness of dough to improve its handling properties. However, salt also inhibits yeast fermentation and the rate of production of carbon dioxide. In the production of steamed products, salt is usually added to the savory filling for steamed buns and or sprayed on the extended dough layers for steamed rolls, but only occasionally added to the dough. Huang and Quail (1997) found that the addition of up to 1% salt improved the skin color more markedly for steamed bread made from medium flour than strong flour. Over this amount, salt badly affected the skin color of steamed bread made from strong flour, which confirmed the result found by Kruger and others (1992). However, this effect was not observed in the medium flour. An addition of 0.25% salt significantly improved the softness of steamed bread crumb. At salt levels over 0.5%, however, crumb softness was significantly decreased. Salt also affects the water absorption of dough. The addition of 2% salt will decrease water absorption of the dough by 3% (Liu 2005).

Dough preparation

In this section each stage of dough preparation and related equipment is discussed in terms of its function and influence on steamed bread quality. The sponge and dough procedure was traditionally used for steamed bread production. Steamed bread doughs were hand mixed and fermentation lasted 3–4 h in winter and > 1 h in summer (Anon 1982). In the past, overnight fermentation was often used (Liu 2005). As full fermented dough is sour, it needs to be neutralized. The dough is then divided, molded, proofed, and steamed. However, a new processing technique called the "no-time' dough procedure has been developed and is widely used in small factories and workshops. In this one-step fermentation procedure, all the ingredients are mixed to the optimal extent, sheeted, divided, molded, proofed, and steamed. This procedure includes one step fermentation (Figure 31.10).
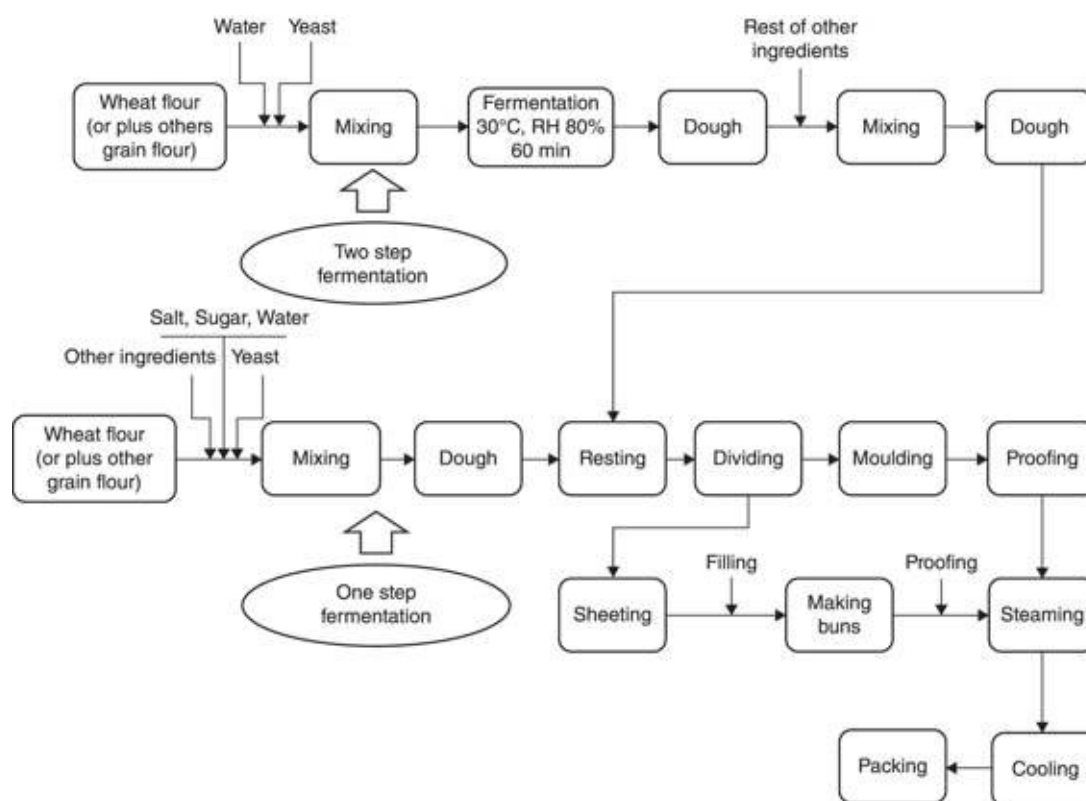
Figure 31.10 The two basic processing procedures popularly used in China today. Source: Liu 2005.

Based on traditional processing, another popular processing procedure called a two-step fermentation procedure has also been developed. It consists of two fermentation steps and mixings (Figure 31.10).

Ingredient preparation

Preparation of ingredients for dough requires sifting of dry materials to break up lumps and to ensure that no foreign matter is included in the dough; weighing each ingredient so that it is in the correct ratio; and monitoring ingredient temperature to ensure the final dough temperature is within the required range. The installation of a bar magnet in the screening apparatus is required to remove any metal impurities. Small or trace amounts of ingredients need to be dissolved or suspended in water rather than added directly to flour.

The sequence of adding ingredients is another factor which may affect the quality of steamed products. For the instance, if the two-step fermentation procedure is used, water, sugar, and improver are added and mixed. Milk powder and instant active dry yeast are added to flour and blended, and then the water is added. In this way the yeast will not come into direct contact with cold or very warm water and the milk powder will not become lumpy by direct contact with water. Fat is added when the dough has formed, but not developed. Salt is added 5–6 min before the completion of mixing when the gluten has not fully developed.

Dough mixing

Mixing is an important step for the final quality of steamed bread. The purpose of mixing is to:

- blend the dry ingredients;
- hydrate the ingredients to form a homogeneous dough;
- develop gluten into a uniform net work with appropriate consistency;
- entrap and disperse finely divided air bubbles throughout the dough.

Dough consistency

The consistency of the dough affects the handling characteristics and the final quality of steamed bread. Consistency is mainly controlled by water addition, but is also affected by flour quality, dough temperature, and dough development. Compared to pan bread, the optimum dough consistency for steamed bread is "tight". This is not only essential to the machining of steamed bread dough, particularly sheeting, but also to the shape and texture of steamed bread. Dusting flour is often used to smooth the operation during processing.

Water addition

Dough used for production of Chinese steamed bread contains less added water (10–15% less) than European-style bread (Huang and Moss 1991). In traditional European-style wheat flour bread, the total amount of water added to the dough usually varies between 55 and 65% of flour weight. For Chinese steamed bread, however, less water is added to the dough as Chinese prefer a rather chewy bread texture (Faridi and Rubenthaler 1983; Lukow and others 1990; Lin and others 1990). Typically, the amount of added water is about 50% for southern style and 45% or lower for northern style Chinese steamed bread (Huang and Miskelly 1991; Su 2005). The addition of water for steamed bread also varies with flour properties and the final consistency of dough required by the different styles of steamed bread. The main factors that influence the water absorption capacity of the flour are protein content, degree of starch damage, and bran content (Quail 1996).

Huang and others (1993) verified that 70% of Farinograph water absorption (FWA) was the optimum for northern style steamed bread prepared using the optimized laboratory procedure, while 80% of FWA was the optimum water addition for southern style steamed bread (Huang and others 1998). Su (2005) reported that 80% of FWA, 72% of FWA and 65% of FWA were used for the preparation of soft firmness type steamed bread (southern style), medium firmness type of steamed bread (northern style) and hard firmness type of steamed bread, respectively. Liu (2005) stated that 36–42% water addition was used for both the rapid

"no-time" dough procedure and the rapid "sponge and dough" procedure (two-step fermentation procedure) for industrial production of steamed bread.

Mixing equipment

In dough mixing, the basic and by far the most useful work is accomplished by the kneading action of the mixing elements. The design of the modern dough mixer ensures that these machines blend, combine, compress, fold, stretch, and push the dough ingredients into their final state of desired dough development.

Mixer types and their characteristics

There are two positions of the revolving axis of mixers used for steamed products: vertical and horizontal (Liu 2005). Most mixers with a large capacity are horizontal (maximum: 50–200 kg), and these are widely used in China. Medium-intensity mixers are the most suitable for steamed products. They include the horizontal type, the vertical type with spiral action, and continuous dough pushing mixers. These latter mixers usually require < 15 min to achieve good dough development. A considerable amount of heat is generated during mixing, so a supply of chilled water is recommended to control the temperature of the final dough. High-intensity mixers are those which can completely develop doughs within 4 min, and such machines may be called mechanical dough developers. Some of these mixers work under vacuum. Cauvain and Huang (1986) applied the Chorleywood Bread Process (CBP) to steamed bread production with a Tweedy 35 high-speed mixer fitted with a water jacket. This work showed that it was possible to produce steamed bread by CBP, which offers a number of advantages over the standard fermentation processes for producing Chinese steamed bread.

Mixing speed

Huang and others (1998) found that mixing intensity affected the specific volume and the surface smoothness of steamed bread to a similar degree. Specific volume increased up to a mixing speed of 60 rpm for all flours and tended to decrease at speeds > 60 rpm. Strong and medium flours showed a greater response to mixing intensity than weak flour. Based on these results, 60 rpm was selected as the optimum mixing speed when using a Farinograph mixer to prepare steamed bread. The best mixers for steamed bread production should have multiple speeds; low speed (15–30 rpm) and medium speed (60–80 rpm) are usually used.

Dough development mechanism

Huang and Moss (1991) revealed that the microscopic appearance of doughs used for the production of Chinese steamed breads did not show marked changes as mixing progresses. The gluten in steamed bread doughs is not initially pulled away from the starch and subsequently developed into a continuous network as it is for European style bread doughs. Although there is little visible change in dough microstructure, steamed bread quality is still influenced by mixing time. The mechanism of dough development of steamed bread exhibits some similarities to that of noodle doughs (Moss and others 1987). The water addition for noodles is very low (32%) and is also low for steamed bread (42–50%). This reduction in the amount of water available for gluten hydration affects the mechanism of dough development.

Dough development

In conventional mixing, dough development is achieved in six differentiated stages.

1. During the initial stage, the main action is the incorporation of dough ingredients. At this point, the dough is "slack" and rather wet, rough, and sticky to touch.

2. With continuous mixing, the dough enters the "pick-up" stage, during which the gluten structure begins to form. The dough does not stick to the mixing bowl. Dough is still somewhat rough, sticky, and easy to break.

3. As the dough continues to develop it becomes drier and more elastic, and begins to form into a more cohesive mass that slaps the back of the mixer bowl. At this stage the dough is well developed.

4. The dough enters the final "development stage". This involves the readily observable transformation of the dough mass from a somewhat rough appearance to a smooth, satiny sheen. Dough stuck to the mixing bowl will leave as the mixer bar moves past. There is a sound of "pa, pa, …" and the dough sticks around the mixer bar like "spindle".

   When the dough starts to stick to the bottom of mixer bowl, the optimum mixing has been achieved. A small piece of dough can be stretched into a semitransparent membrane of essentially uniform thickness before it ruptures.

5. If mixing continues past the development stage, the dough loses its elastic character and becomes increasingly soft, highly extensible, and sticky. This is called the "let down" stage. More and more dough sticks to the bottom of the mixer and starts to stick to the walls of the mixer as well.

6. Doughs mixed beyond the "let down" stage disintegrate completely. They become slack and runny, losing all their elasticity. They can no longer be used to make steamed products. Disintegrated doughs stick to the mixing bowl.

Control of mixing time

The period required for dough to be well developed varies with different flours. Various factors exert a measurable effect on the initial dough temperature and total dough mixing time; these include differences in starting temperature, water absorption, flour strength, use of salt and fungal enzymes, and mixing speeds.

Dough temperature

Dough temperature affects the fermentation rate and all other subsequent processing. The final dough temperature is determined by the temperature of the initial ingredients, particularly water, and the heat generated during mixing. The water temperature is often used to adjust the final dough temperature.

Floor time

The term "floor time" refers to the period from when mixing is completed to when the dough is divided or sheeted; for steamed products, this period varies between bakeries. Huang and Quail (1997) found that 5 min floor time is appropriate for the production of Guangdong style steamed bread using the optimized laboratory rapid "no-time" dough procedure. Liu (2005) pointed out that 10 min floor time is enough for the industrial production of steamed bread.

Sheeting

Huang and others (1993) observed that sheeting time had strong positive effects on exterior smoothness, interior structure, and the total quality score of northern style steamed bread for both medium and strong flours. The sheeting process improves the quality of steamed bread by removing air trapped in the dough during mixing, developing the gluten network further, making the structure of dough finer, and increasing the white color of the dough. This was achieved in laboratories by passing the mixed dough through a sheeting machine with a controlled roll gap (depending on the size of the dough) up to 20 times. Kneading machines are used to complete the sheeting process in some steamed bread factories. Kneading machines have one or two pairs of rollers and their gap can be adjusted. Sheeting, up to 30 times, was very beneficial to the quality of steamed bread. However, sheeting over 40 times will make the dough sticky (Liu, 2005). Sheeted dough is divided and molded in laboratories. However, sheeting can also be achieved commercially using a molding machine (see the next section).

Molding

Steamed bread

In steamed bread factories, the mixed and floored dough is passed through a molding machine. The dough is cut into small pieces and pushed into the molding machine. Finally the dough pieces are processed into round and smooth pieces with a fine structure (Figure 31.11).

Figure 31.11 Molding steamed bread dough. (Courtesy of D. Miskelly).

Steamed buns

To mold dough into steamed buns, the mixed and sheeted dough is transferred to a lightly floured work surface and kneaded a few times, Then it is rolled by hand into a cylinder 40 cm

long and 4 cm wide. The cylinder is cut into 2.5 cm pieces which are turned on their flat ends and pressed with the palm of the hand to flatten them. Each piece is then rolled with a rolling pin into a 7.5 cm circle with the dough being rotated and the edges being rolled thinner than the center (Huang 1999). With one round held with the palm of the left hand about 1.5 tablespoons of filling is added to the center of the round. The thumb of the left hand is used to push the filling down while pinching and pleating the edge of the round with the thumb, forefinger, and the middle finger of the right hand to enclose the filling. In China and other East and Southeast Asian countries, buns with a sweet filling are usually steamed upside down to identify them as sweet ones. The edge is first pinched and the bun is given a twist to make sure it is tightly closed, before being put closed end down. After steaming, these sweet buns may be marked with a spot of food coloring to further identify them.

Steamed rolls

Steamed rolls are prepared by rolling the fermented dough into a large thin flat shape (round, square or rectangular). A layer of a particular condiment is spread over this dough sheet. It is then rolled and cut into pieces, shaped and then steamed. In general, steamed rolls can be divided into three groups: rolled rolls, folded rolls and stretched rolls. For details refer to Huang (1999).

Fermentation (or proofing)

Before the molded dough pieces can yield a light, aerated loaf of steamed product, they must be fermented for a period of time (Figure 31.12). During this process, the yeast cells act upon the available sugars, transforming them into carbon dioxide gas and alcohol as the principal end products. There are several fermentation procedures currently used in steamed bread factories in China: one-step fermentation and two-step fermentation (see Figure 31.10).

Figure 31.12 Proofing stage of steamed bread, buns and rolls. Courtesy of D. Miskelly.

One-step fermentation

This is also called the "no-time" fermentation procedure. All ingredients are mixed together, sheeted and molded, then proofed and steamed. Virtually all the fermentation takes place in this proofing stage, which takes about 50–80 min. This procedure has the advantage of reducing process time, labor, power, and equipment requirements. There is also a reduction in fermentation losses because of the short fermentation time. The disadvantage of this procedure is that more yeast is used. The steamed bread produced has a firmer texture and much less flavor than those made by traditional methods.

Two-step fermentation

Two-step mixing and two steps of fermentation can be used to produce steamed bread (see Figure 31.10). In the first mixing, about 70% of the flour and 80% of the total water and total yeast are added and mixed for 3–4 min with a final dough temperature of 28–32 °C. After that the dough is fermented at 30–33 °C and 70–80% relative humidity for 50–80 min depending on yeast level, ratio of flour used in the first mixing, temperature, and relative humidity in the fermentation cabinet. The fermented dough is then mixed again with the rest of the flour, water, and alkali solution (0.05–0.1% of alkali). Alkali is used to neutralize the acids produced during the fermentation. The second mixing takes 8–12 min with a final dough temperature of 33–35 °C. The dough is then divided, molded, and proofed for about 60 min at 38–40 °C and 80–90% relative humidity.

This procedure produces dough with a better gluten network and the operation can be closely controlled. It uses less yeast with the steamed bread having a smoother appearance, softer texture, good keeping quality, and better flavor. However, the two-step fermentation procedure requires a longer production time, uses more labor, and needs more equipment and space.

Steaming

Proofed dough pieces are cooked by steaming in bamboo baskets over boiling water at home or in a steaming chamber or cabinet in factories, instead of being baked in an oven. This cooking process resulted in huge differences between steamed bread and baked bread.

Changes in moisture

During steaming, the moisture content of the steamed bread increases, particularly during the first 10 min of steaming. Steam increases the moisture content of steamed bread, while the increasing bread temperature in turn accelerates evaporation of moisture from steamed bread.

Changes in volume

The volume of steamed bread increases drastically in the first 5 min of steaming. It was observed that small bubbles appear on the surface of steamed bread during the first 5 min of steaming if the air bubbles trapped during mixing were not removed by sheeting. These small bubbles ruptured when the steamed bread was removed from the steamer, leaving blisters on the skin of steamed bread.

Control of steaming conditions

It was found that steam generation rate is very important to the quality of steamed bread (Huang and others 1993; Chen 2007). A steaming rate that was too low did not produce good-quality steamed bread; the bread had a smaller volume, poor texture, and sticky eating quality. However, a steaming rate that was too high also resulted in quality problems such as blisters, dimples, and jelly port on the surface of steamed bread and even shrinking of the steamed bread. These problems are more obvious in steamed bread made from flours with strong dough strength. It was recommended that 155 $g/m^3/min$ steaming rate is suitable for a steamer in laboratory-scale steamed bread production (Huang and others 1993). This steaming generation rate is only 0.0001 MPa when four 100 g pieces of steamed bread dough are steamed for 20 min. Requirements for steaming rate vary according to the size of steamed bread, amount of steamed bread dough tested in the same batch, steaming time, and variety of products. A steam rate of 0.003 MPa is suggested for use when over eight pieces of steamed breads of the same size are steamed for 20 min in laboratories. A higher steam generation rate than this, for instance 0.03 MPa, is definitely detrimental to the quality of steamed bread. Chen (2007) pointed out that the steam generation rate had great influence on the quality of steamed bread. A high steam generation rate resulted in the shrinking of steamed bread, particularly for steamed bread made from flour with high and medium dough strength, but not to that made from flour with weak dough strength.

For industrial production, Liu (2005) recommended that a steaming rate between 0.01 and 0.06 MPa was suitable for a steam chamber in factories. Steaming times vary according to the size of the steamed bread, steam rate, and variety of products. Generally, 26–27 min steaming time is enough for steamed bread production of 135 g dough if the steaming rate is between 0.02 and 0.04 MPa (Liu 2005).

Cooling and packing

Cooked steamed bread needs to be cooled down before packing. Moisture loss occurs when steamed bread is exposed to air. The decreased temperature and lower air pressure that occur when steamed bread is taken out of the steamer, accelerate the process of migration of moisture from the surface of steamed bread to air and from the center of steamed bread to the surface. The cooling rate of steamed bread depends on the temperature difference between steamed bread and the room, relative humidity, and the size of the products. It is harmful to the quality of steamed bread if too much moisture is lost, as the skin cracks and the bread becomes firmer in texture. Generally, the requirement is to cool the center of steamed bread to 50–60 °C before for packing. Packing on time is a good practice for maintaining the quality of steamed products, delaying aging, preventing contamination and further damage, as well as increasing the value of the products. Polyethylene bags are the most popular packaging materials for the steamed products. Re-steaming is another good practice that improves the quality of steamed products prior to consumption.

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Part 6
Other Bakery Products

32
Cake Manufacture

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Introduction

For centuries, cake making changed very little. The 16th century spice cake, the 18th century nun's cake, and even the rich pound cake of the colonial days required long hours of labor. Old "receipts" read, "take a half a peck of fine wheat-flour … three pounds of refined sugar… dry them by the fire… take four pounds of butter, beat it with a cool hand, then beat thirty-five eggs," and so on. Later recipes called for smaller amounts, but the method of mixing was essentially the same (Anon. 1998).

There are a variety of cake products with a broad range of formulations. Ingredients such as tour have improved through processing; therefore, cakes contain higher levels of shortening, sugar, eggs, and milk. The modern cake is characterized by a sweet taste, short and tender texture, and pleasant flavors and aromas (Pyler 1988a).

The two basic categories of cakes—foam and shortened—are distinctly different in their preparation and problems. The shortened-style cake (pound cake, yellow cake, chocolate cake, etc.) has a crumb structure derived from a fat-liquid emulsion that is created during batter processing. Foam-style cakes (angel food, sponge, chiffon) depend on the foaming and aerating properties of eggs for their structure and volume.

The quality of a cake is dependent on several factors. The selection of ingredients and the knowledge of their function is the first step towards a quality product. However, there is much more to making an acceptable product. The cake recipe is a balanced formula, and measurements must be precise. The final step is adherence to optimal mixing and baking procedures. This chapter will deal with aspects of cake production as a function of ingredients, mixing methods, and baking requirements, focusing on their effect on cake quality.

Ingredients: functional role

The ingredients in a cake formula are present in proportions designed to yield a good quality product. Each ingredient contributes to a particular aspect of cake quality: tenderness, structure, moisture, or flavor. Some ingredients will serve a dual purpose, as will be illustrated below. No matter what ingredient is selected for the cake, the quality of the finished product is the primary end. Any deviation from the proper ingredient, its amount, or the proper mixing method will affect the cake.

Shortening and fat substitutes

Shortening

Shortening is the primary tenderizing agent in cake. Shortening also imparts moistness. A layer cake made with oil as the shortening gives the impression of a moister crumb than a cake from the same formula made with an emulsified plastic shortening (Stauffer 1998). Keeping quality and, depending upon the type of shortening, flavor round out the attributes. Pound cakes prepared with butter possess a flavor that cannot be equaled by those prepared with a plain shortening.

Soybean oil and cottonseed oil are the principal raw materials for hydrogenated vegetable oil shortenings in the United States (Matz 1992a). Hydrogenation is a process whereby hydrogen ions are added to the double bonds of the polyunsaturated fatty acids, and turning the fat saturated and solid. It has been established that hydrogenation causes trans fatty acids, and research has been undertaken to develop other methods for the fat manufacturer. One method suggested is interesterification, whereby the plastic fat is created by simply transferring a saturated fatty acid onto the fatty glycerol to create the β'crystal arrangement of the fatty acids that is necessary for a plastic fat (Wainwright 1999).

The hydrogenation process creates a plastic fat that is important to the creation of a cake batter that traps air bubbles and produces a fine-grained and a high volume cake. During mixing, fat and sugar are combined and mixed (creamed). During this step, the air is dispersed in the solid phase. In the presence of an emulsifier, such as monoglyceride, these bubbles are divided into numerous small air cells by the action of the beater. The shortening must be not only solid, so that the bubbles do not escape, but also plastic, so that it can fold around each air pocket (β' crystal structure of fatty acids in the fat).

The emulsifier incorporated into the fat is also important in promoting air dispersion. Batter includes a liquid, and since fat is insoluble in a liquid the emulsifier helps to maintain a homogeneous mixture. An emulsified shortening containing monoglyceride at 4.5% would be typical for cake shortening (Stauffer 1998). Other emulsifiers such as Polysorbate 60, sorbitan monostearate, and plastic mono-and diglycerides give good results.

When a one-stage process (all ingredients are added at once) is used in mixing, the air is entrapped in the water phase rather than in the shortening. To form the air-in-water foam an α-tending emulsifier in the shortening is required. The most common emulsifiers used at the 7–10% level in the plastic fat are propylene glycol monoesters (PGME) and acetylated monoglyceride [AcMG] (Stauffer 1998).

Cakes made with oil as the shortening are more tender than those made with a plastic shortening. The cake gives an impression of moistness when eaten, even after storage for a week or more (Stauffer 1998). In commercial cake production, unfortunately, oil cakes are often too tender to withstand the necessary handling along the production line. However, tenderness is highly desirable from the consumer's standpoint, so packaged cake mixes for home use are usually made with oil for the shortening. Again, α-emulsifiers are used to stabilize the foam created by proteins contributed by eggs and flour. Propylene glycerol monostearate (PGMS) and stearic acid (80:20) help to form a strong film (Stauffer 1998).

Cakes typically contain 15–25% fat on a batter weight basis. Therefore, high-ratio shortenings (containing mono- and diglycerides) are recommended. This type of shortening significantly enhances the structure of the cake batter, thus permitting the sugar-to-flour ratio to be increased and, consequently, improving cake quality (Wainwright 1999).

Fat substitutes

Interest in healthy eating has risen, and the search to lower calories in cake has been ongoing. The reduction of fat in cake has been researched, but reducing the amount of fat reduces not only calories, but also cake quality. There have been various fat substitutes that have been investigated to meet the demand for a reduced-fat cake. These fat substitutes can be categorized as protein-based, carbohydrate-based, or fat-based.

A popular protein-based fat substitute developed is called Simplesse; it is tiny drops of an aqueous solution encapsulated in microscopic vesicles of egg white or milk protein. The material has a viscous, lubricating texture and appears to function very well in certain limited applications as an ingredient in no-fat ice cream. It would probably be of little or no use in a cookie dough or batter (Stauffer 1996). During heating, these proteins lose their spherical shape and thus their ability to act as a lubricant.

Carbohydrate materials have been suggested as fat mimetics. Some that have been used are polydextrose, maltodextrins, tapioca dextrins, potato starch, microcrystalline cellulose, and gums such as alginates, xanthan gum, carrageenan, and locust bean gum. Maltodextrin solution can be concentrated to mimic shortening. This maltodextrin solution can be used along with microcrystalline cellulose as a partial replacement for the fat in a shortened-style cake (Conforti and Archilla 2001). N-flate also has been developed; it is a blend of emulsifiers, modified food starches, and guar gum in a nonfat milk base. N-flate is used as a partial fat replacer in cakes, muffins, and cookies. It yields a layer cake, for example, with good volume, grain, and mouthfeel characteristics (Stauffer 1996).

Fat-derived substitute (sometimes called engineered fats) include sucrose polyesters, polyglycerol esters, triglyceride esters of alpha-substitute carboxylic acids, and alkyl glycoside polyesters. Probably the most work has been done with sucrose esters. Olestra is the trade name for sucrose combined with six, seven, or eight long-chain fatty acids. This substance is claimed to be not absorbed in the human intestine, so it is devoid of calories when used as a component of the diet. Sucrose polyesters are differentiated from other fat substitutes by their reasonable stability at high temperatures. Other possibilities have been listed by Nelson (1990).

Another approach is to make triglycerides that have the functional properties of ordinary fats but are metabolized somewhat differently, giving a lower caloric yield per gram. Salatrim is a

monostearin esterified with short-chain acids (acetic, propionic or butyric). Salatrim (which has several different forms, depending on the ratios of the short-chain fatty acids used to make it) has plastic properties roughly equivalent to those of all-purpose shortening or a filler fat. It has been used to substitute for these fats in products (Stauffer 1996).

Because the "ideal" fat substitute does not exist, a systems approach to reduced-fat or low-fat food formulations has been proposed. Simply put, a systems approach uses a combination of different ingredients that may or may not belong to any of the classes of fat replacers and requires a basic knowledge of ingredient technology to formulate desired products. The system may contain emulsifiers, fat substitutes or mimetics, fibers, water control ingredients, and/or flavor and bulking agents. Water or moisture control poses one of the greatest challenges in formulating reduced-fat snack or baked goods. In these systems water is used to replace fat, to increase bulk, or for functionality (Akoh 2002).

Flour

Flour is the final product of milling a mixture of wheats, or single wheats, cleaned, conditioned, and mixed to form grist, which will yield flours suitable for the various requirements of the baker. The quality of the flour is dependent on the quality of the wheat, the method of milling, the length of the extraction, and the level of chemical treatment (chlorination).

Flour provides structure, texture, and flavor to baked products. Starch is one of the components in flour that strengthen the baked item through gelatinization (changes that starch undergoes when subjected to moist heat), and one of the factors that contribute to crumb. Crumb is partially created during baking and is dependent on the number and size of the air cells produced, the degree of starch gelatinization, and the amount of protein coagulation (Jacobson 1997).

When mixed with water, protein from the flour forms an elastic network known as gluten. The two proteins are gliadin and glutenin. Glutenin is responsible for the elasticity of the dough while gliadin is responsible for dough extensibility. Therefore, gluten is both elastic and plastic. The ability of gluten to expand is due to the inner pressure of gases such as air, steam, or carbon dioxide combined with glutenin's elasticity and gliadin's fluidity (Sontag-Strohm et al. 1996).

Milling or grinding is the process in which the grain kernel is first freed of its bran and germ and then has its endosperm ground into a fine powder known as flour. Any grain can be milled, but wheat flour dominates the market (Brown 2000a). Milling today consists of five basic steps: breaking, purifying, reducing, sifting, and classifying. In breaking, special machinery equipped with break rollers removes the bran and germ layers from the grain's endosperm. Each succeeding pair of steel break rollers is set closer together to remove more of the bran and germ. The result is known as break flour. Break flour still has some of the bran attached to the endosperm layer. To further remove this, the flour is moved through containers where blowing air currents remove any remaining bran. The endosperm, thus freed, or purified, from the whole grain and now free of bran, is known as middlings. At the reducing stage, 10–15 smooth-surfaced reduction rollers grind the middlings into flour. To prevent the starch granules from being damaged, the spaces between the rollers are progressively reduced.

The flour is then sifted in streams, and this sifting determines how the flour is classified. Flour streams range from fine or first break to coarse or clear, and the types of flour obtained range from patent flour to straight flour. Patent flour is divided into long, medium, or short patents depending on how much of the total endosperm was milled. Short patents come from the center of the endosperm, are high in starch, and are best for making pastry flour. Long patents contain more protein from outer areas of the endosperm and are preferred for the production of bread flour. Clear flour, which is left over from patent flour, is further subdivided into fancy clear, first clear, and second clear. The coarser clear flours are primarily used for all-purpose flour. The quality and grade of the final flour is determined by which streams were combined in its production. The protein content varies according to the origin of the stream and the type of grain used (Petrofsky and Hoseney 1995).

Wheats differ in their protein content. Soft wheats have the least protein and highest starch content, making them ideal for the tender, fine crumb cakes and pastries. Hard wheats, with their high protein content, are preferred for yeast bread (Hoseney and Rogers 1990). For cakes, the flour of choice is cake fl our. It is pure white and has a very fine, silky soft texture. Its low protein content of 8% and small particle size compared with all-purpose flour results in less gluten formation, which gives the cake a fine grain, a delicate structure, and a velvety texture. Cake flour is also treated with chlorine gas (this is not allowed in the United Kingdom), which lowers the pH from about 6.0 to 5.0, bleaches the plant pigments, and improves baking quality (Fustier and Gelinas 1998). Chlorination increases the water absorbency of the starch and thus contributes to a firmer, smaller crumb and a stable product. This is especially important with the high amount of sugar in the cake formula; since sugar is a good competitor for water, chlorination aids the starch in this capacity (Conforti and Johnson 1992).

All-purpose flour can be used to make cakes, but the cakes may have a slightly coarser texture and lower volume (Yamazaki and Donelson 1972). The protein content of the all-purpose flour averages about 11%, while bread flours that need strong gluten development contain 12–14% protein. Blending hard and soft wheat flours yields flour that can be used for all purposes-breads, cakes, or pastry. Despite what appears to be a uniform product, the actual protein content of all-purpose flour may differ from region to region and brand to brand. Regional differences have influenced manufacturers to place more protein in flour sold in the northern United States, where yeast breads are more popular, than in flour sold in the South, where biscuits requiring a softer flour are more routinely consumed. All purpose flour may or may not be bleached.

Self-rising flour is usually all-purpose flour, but cake flour could also be self-rising. The leavening agent and salt are added to the flour. The leavening agent is a baking powder (baking soda combined with a salt, monocalcium phosphate). One cup of self-rising flour contains about $1\frac{1}{2}$ teaspoons baking powder and $\frac{1}{2}$ teaspoon salt.

Sugar and sugar alternatives

Sugar

Aside from contributing sweetness, sugar also influences the volume, moistness, tenderness, color, appearance, and calorie (kcal) content of baked products. There are two principal

sources of commercial sucrose—sugar cane and sugar beets. Cane must be brought to the mill and crushed as soon as possible to reduce exposure to microorganisms that would quickly begin to metabolize the sugar. To obtain sugar from sugar cane, 12- to 18-month-old cane is crushed between rolls. The mixture is heated to coagulate proteins, including the hydrolyzing enzyme invertase. The mixture is filtered and concentrated under reduced pressure at a carefully controlled temperature to 50% solids. When crystals of about 300 μm diameter develop, they are removed by centrifugation and given a brief wash. The mother liquid is further concentrated to obtain another crop of crystals. Such concentration and crystallization is conducted until impurities build up to the point where the remaining sucrose will not crystallize. This raw sugar is brown and is shipped to refining mills for purification. There it is dissolved and mixed with lime and phosphate to further precipitate and flocculate impurities. The mixture is clarified and deodorized by centrifugation and by filtration through diatomaceous earth and charcoal. Final crystallization under reduced pressure yields pure white table sugar (Whistler and Be Miller 1997b).

The operation of making the crystals different sizes is done in the vacuum pan. If large crystals are wanted, then large and heavy charges of syrups are placed in the pans at long intervals so that the crystals can grow during boiling. On the other hand, if fine crystals are wanted the charges of the syrup are light and frequent. Thus, in the refining of sugar, three or four grades are obtained. The top grades are at least 99% pure sucrose. The second grades are slightly inferior. The third and fourth grades contain a few impurities, have generally a yellow or dark color, and are sent to the market as partially refined sugars, known as third or fourth pieces. After sugar is refined, it is impossible to tell whether it has been derived from sugar cane or sugar beets (Bennion and Bamford 1973a).

Brown sugar is used often in cakes. Commercial brown sugar is made by simple crystallization from lime-treated but incompletely purified cane juice or, more often, by treating white sugar crystals with molasses to give them a brown coating of the desired thickness. Grades range from light yellow to dark brown. They are high in ash and moisture and are slightly sticky, resulting in their being called "soft sugar" in the industry. Beet sugar molasses is not suitable for brown sugar production (Whistler and Be Miller 1997b).

Sugar serves multifunctional roles in cake making. One important function is that it increases the volume of cakes by the incorporation of air into the fat during creaming. During baking sugar raises the temperature at which gelatinization and coagulation occur, which gives the gluten more time to stretch, thereby further increasing the volume of the baked product and contributing to a finer, more even texture (Bean and Yamazaki 1978). The hydroscopic or water-retaining nature of the sugar increases the moistness of the baked cakes. This is very evident when brown sugar is used in the formula. Brown sugar can be used in some low-fat products because of its hydroscopic nature, which can increase the moistness in the cake. Sugar competes with starch for the available water necessary for the hydration of proteins and starch and eventually gluten development. Finally, sugar helps to brown the crust through caramelization and Maillard browning. Caramelization is a process in which sucrose alone is involved in a series of chemical reactions brought on by the baking temperatures (Camire et al. 1990). Maillard browning involves two components, proteins and carbohydrates. Flour, containing both proteins and carbohydrates, and sugar, also a carbohydrate, contribute to a chemical reaction that produces a brown crust (Whistler and Be Miller 1997a).

Sugar alternatives

Alternatives to sugar are available and sometimes serve as substitutes for sugar in baked products. There are two types: nutritive sweeteners and non-nutritive sweeteners. Other than sucrose, nutritive sweeteners include fructose, glucose (dextrose), syrups (corn syrups, high fructose corn syrups [HFCS], maple syrup), honey, molasses, sugar alcohols (D-glucitol, mannitol, hydrogenated syrups), maltodextrins, neosugar, and aspartame. Aspartame, a dipeptide ester is characterized as a nutritive sweetener by the U.S. Food and Drug Administration (FDA) because, on an equal weight basis, it has approximately the same caloric content as a carbohydrate. However, since about 200 g of sucrose can be replaced by 1 g of aspartame because of the greater sweetness potency of aspartame, it effectively functions as a nonnutritive sweetener.

Choice of a suitable polyol for use in bakery products to achieve a finished sweet product has been studied. Sorbitol, mannitol, maltitol, and hydrogenated hydrolysates are most commonly used, singly or in various combinations (Ikawa 1998, Desbonnets 1998, Lin et al. 2003).

Only four alternative sweeteners are currently approved by the FDA for use in the United States: saccharin, aspartame, acesulfame-K, and sucralose. Two relatively new sweeteners are alitame, which is pending FDA approval as of this writing, and neo-tame, which has recently been approved. In addition, cyclamates, which had been approved but were later banned in the United States as a potential carcinogen, are trying for a comeback.

One drawback of alternative sweeteners is that they do not provide the important functional character of sugar: bulking, binding, texturing, and fermenting. However, certain compounds can be added to foods to compensate for bulking. These compounds include cellulose, maltodextrin (also for its binding property), the sugar alcohols, and polydextrose. Polydextrose provides a texture similar to sugar, but the amount required may have an adverse effect on texture in high-ratio cakes (cakes with a higher amount of sugar and liquid to flour) (Pateras and Rosenthal 1992).

Leavening agents

The verb *leaven* means to "lighten," to "rise," such that, during baking the product rises in volume and is not heavy but light in texture. Therefore, volume and texture are formed in the cake.

Leavening agents are characterized as air, steam, and CO_2 (carbon dioxide). Carbon dioxide is derived from either a biological source or chemical source. Yeast would be considered a biological source and is used in breadmaking. Since this discussion is not considering yeast products, the contribution of yeast will not be considered here. Chemical sources of CO_2 in a cake batter are baking powder and baking soda. These ingredients are essential for a risen product and will be described below.

The initial leavening agent incorporated into the cake batter is air. Simple manipulation of the ingredients and batter incorporates air. Air is incorporated by the simple action of sifting together the flour and other dry ingredients (salt, baking powder, and/or baking soda). In many angel food cake recipes, the sifting of flour and sugar at least four times is recommended to ensure proper air incorporation. Another method that incorporates air is

"creaming" of fat and sugar. The fat (plastic fat) helps in the incorporation and trapping of air and in distribution of air cells into small units in the batter. During heating, the air is released and the product rises. Beating egg whites, especially important for foam-style cakes, is another example of incorporating air into the batter. Egg whites warmed to room temperature are able to hold onto the air that is beaten into them. Whole eggs are beaten into a foam for some cakes (genoise, for example). Usually the eggs are warmed over a water bath and beaten at the same time in order to trap air during beating. Whether it is a whole egg or egg white, the foam must be baked immediately because if it stands for any length of time air is lost and so is the volume of the cake. Careful folding of the ingredients is a manipulation technique that must be meticulously observed. Overmanipulation of the foam causes loss of air and a heavy, low volume cake.

The liquid in the recipe forms steam. Whether the liquid is water or milk, when it is heated steam is produced and the cake rises. Liquid has other functions in the recipe (see the next section). Egg whites are made up of water (~88%). A foam-style cake, particularly angel food cake, relies on the steam produced by the egg whites. Therefore, a true foam-style cake is leavened predominately by air and steam.

Chemical leavening involves baking powder and baking soda (sodium bicarbonate). When either of these compounds comes in contact with a liquid and heat, a chemical reaction occurs that produces CO_2 and the product rises. When raised to the proper height, the product texture is porous, and a light but not heavy product is produced.

Baking soda (sodium bicarbonate) chemically yields CO_2 when it reacts with an acid in the recipe. Examples of an acid would be buttermilk, sour milk, cocoa, yogurt, sour cream, applesauce, honey, brown sugar (contains organic acids), or fruit juice. Up to ¼ teaspoon baking soda per cup of flour is recommended. The acid reacts with the baking soda and the following reaction results:

$$NaHCO_3 + HX \rightarrow NaX + H_2CO_3 \qquad (1)$$

$$H_2CO_3 \rightarrow H_2O + CO_2 \uparrow \qquad (2)$$
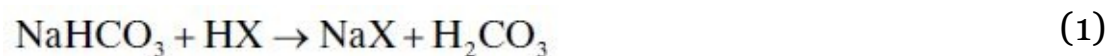
The acid (HX) reacts with the sodium bicarbonate ($NaHCO_3$) in the presence of water and heat, and an intermediary product is formed: carbonic acid (H_2CO_3). Carbonic acid then yields water and carbon dioxide, and the product rises.

If sodium bicarbonate is used without any acid then the following reaction will occur:

$$2NaHCO_3 \rightarrow Na_2CO_3 + 2H_2O + CO_2$$
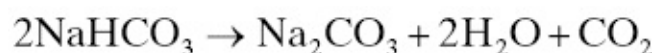
Carbon dioxide is still formed, and the cake will still rise, but sodium carbonate (Na_2CO_3) is formed. Depending on the amount of baking soda that was used initially, the sodium carbonate formed will affect the flavor and color of the product. Usually a soapy flavor and a yellow color will be the outcome.

When baking powder is used, it is not necessary to use an acid because the acid is already built into the mixture. The inert filler in baking powder absorbs any excess moisture in the

air, which would otherwise cake the powder and/or reduce its potency.

The two types of baking powder are fast or single-acting powder, and slow or double-acting baking powder. A flour mixture made with fast/single-acting baking powder should be handled quickly and efficiently and placed in the oven as soon as possible, because it starts to produce carbon dioxide as soon as water is added. Any delay allows the carbon dioxide to escape and decreases the ability of the mixture to rise. Approximately $1\frac{1}{2}$ to 2 teaspoons of single acting baking powder are required for every cup of flour.

Many commercial bakers use double-acting baking powder (sodium aluminum sulfate [SAS]-phosphate powder), which reacts twice: first in the mixing bowl and then in the oven (heating). Approximately 1 to $1\frac{1}{2}$ teaspoons baking powder are required for every cup of flour.

The reactions that follow illustrate how double-acting baking powder will react:

$Ca_3(PO_4)_2 + 8H_2O + 8CO_2$ tricalcium water carbon

phosphate   dioxide

Step 1

$$8NaHCO_3 + 3CaH_4(PO_4)_2 \rightarrow$$

baking soda   momocalcium phosphate

$$4Na_2HPO_4 + Ca_3(PO_4)_2 + 8H_2O + 8CO_2$$

disodium phosphate   tricalcium phosphate   water   carbon dioxide
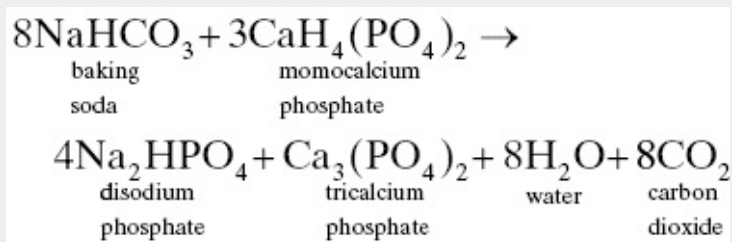
The initial reaction occurs at room temperature when the baking powder is moistened, due to the presence of phosphate (PO_4), usually monocalcium phosphate [$CaH_4(PO_4)$]. A light, bubbly, viscous batter is produced. The acid is converted into a variety of phosphate salts, some of which may react with each other. The rate of release of carbon dioxide for this initial reaction is very fast (60% within the first 2 minutes of mixing) (Freeland-Graves and Peckham 1995). If there is a delay when the cake is to be baked, it is best to cover the batter with plastic wrap and refrigerate it. This will slow the above reaction.

$$2\text{NaSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} \xrightarrow[\text{heat}]{}$$ (a)

$$\underset{\substack{\text{sodium}\\\text{sulfate}}}{\text{Na}_2\text{SO}_4} + \underset{\substack{\text{aluminium}\\\text{hydroxide}}}{2\text{Al}(\text{OH})_3} + \text{H}_2\text{SO}_4$$ (b)

$$6\text{NaHCO}_3 + 3\text{H}_2\text{SO}_4 \rightarrow$$
$$3\text{Na}_2\text{SO}_4 + 6\text{H}_2\text{O} + 6\text{CO}_2$$
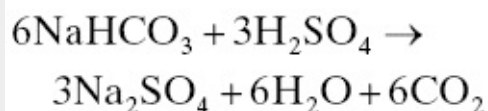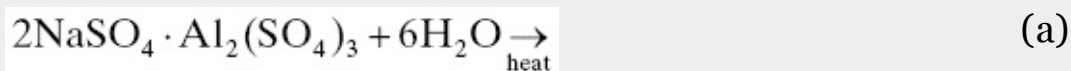
The second reaction, which occurs when the batter is heated, has two stages. The first stage (a) occurs when sodium aluminum sulfate [$\text{NaSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3$] is solubilized in hot water and produces sulfuric acid (H_2SO_4). In the second reaction (b) the sulfuric acid reacts with the baking soda (NaHCO_3) that has not been neutralized by the monocalcium phosphate [$\text{CaH}_4(\text{PO}_4)_2$]. Carbon dioxide is produced in this reaction and the cake rises.

The usual amount of double-acting baking powder used is $1\frac{1}{2}$ teaspoons (8 mL) to 1 cup (240 ml) flour (Freeland-Graves and Peckham 1995).

Liquid

Whether the liquid in the recipe is water, milk, or buttermilk, it performs several functions in the recipe. Liquid hydrates the starch in the tour and when heated causes gelatinization of starch. Liquid dissolves the ingredients, especially sugar, during mixing and baking of the cake batter. It is also essential for the release of carbon dioxide from either baking powder or baking soda. Liquid also produces steam and therefore, along with carbon dioxide, aids in leavening. Usually milk is a popular liquid for use in cake batter. In addition to contributing water, milk adds flavor and nutrients (complete protein, B-vitamins, and calcium) and contains certain compounds that help produce a velvety texture, a creamy white crumb, and a browner crust. The lactose in the milk participates in the Maillard reaction (see Sugar section, above), resulting in a brown crust.

Eggs

The function of eggs when used in a cake batter may be defined as the following (Bennion and Bamford 1973b): (1) moistening, due to the large amount of moisture (water) present; (2) aerating, due to the ability to form a foam when whisked, which entangles large quantities of air; (3) enriching, due to the presence in the yolk of a fairly high proportion of fat; (4) emulsifying, due to the presence of lecithin in the yolk; and (5) structural, due to the presence of the proteins in both the yolk and the white that coagulate upon heating. In addition, eggs increase the food value of the product and impart a better color and appearance to the finished product.

Egg whites

The egg white, or albumen, consists chiefly of a complex mixture of proteins, such as albumin, globulins, and others, and about 0.5% of mineral salts. This liquid portion is enclosed in firm fibrous material, which forms membranous cells throughout the mass. The firmer or more jellylike the whites are, the fresher they are. Aging or staling of the white causes a breakdown in the protein, causing a watery white. When egg whites are whisked, they give rise to an assemblage of small air cells. This is because the membranous matter provides a structure on which the protein solution can form thin cells in which air is entrapped. Traces of egg yolk, oily substances, or flour will break the filmy cells as fast as they are formed when whites are whisked. The stability of the egg white foam is largely influenced by the pH of the whites. The lower the pH, the more stable the foam. Weak and watery whites are deficient in membranous matter and are difficult to whisk up.

Sugar is added to the egg white foam to form a meringue. The addition of sugar stabilizes the foam. When beating egg whites, the whites go through four stages: foamy, soft peak, stiff peak, and dry. At the dry stage, the egg whites become dry and brittle, and at the same time, the cells become overstretched. When this occurs it is difficult to fold in the ingredients, and the cake will not rise. Usually the cells are overstretched and will collapse. Some cakes, such as angel food, call for the addition of sugar to the egg white foam. When sugar is added a meringue is formed (this is known as the meringue method). Cream of tartar is added to the egg whites during the foamy stage when the whites are being whisked. Cream of tartar is an acid, and lowers the pH of the whites, thus stabilizing the whites. Sugar is added during the soft peak stage (peaks fall over when beaters are removed). Sugar is added gradually and then beating continues until the peaks are stiff and shiny. Sugar stabilizes the meringue, and there is no danger of overbeating the whites.

Egg yolks

The yolk of an egg is more valuable as a food than the white in that it contains minerals and vitamins. Yolks cannot be beaten as stiff as whites, owing to the presence of so much fatty matter. They can, however, be whisked to quite a reasonable sponge, as is done when using the separated sponge method popular with sponge cakes (see Mixing Methods for Foam-Style Cakes: Sponge Cake, below).

Summary

Ingredients play an important role in creating an acceptable product. Whether alone or together, each ingredient contributes an important quality to the finished cake. Flour, liquid, sugar, leavening agent, eggs, and fat are present in a proportion that when properly mixed produce a quality product.

The main attributes of a cake are *structure, texture, moistness, color* (brown crust), high *volume* and a sweet *flavor*. Flour is one of the main ingredients that contribute structure and texture to the cake. Another major ingredient, sugar, contributes sweetness, but at the same time affects volume, adds moistness, and improves color. Fat is another ingredient that *tenderizes*, increases volume through the creaming process with sugar, and contributes flavor and structure. Eggs contribute structure, color, and aid in leavening (volume). Chemical leavening agents (baking powder and/or baking soda) increase volume and contribute to crumb and texture. Finally, liquid hydrates the flour, gelatinizes the starch for structure, serves as a solvent for the dry ingredients, and contributes to *leavening* (steam and CO_2). The majority of the ingredients share similar quality characteristics. That is why it is important to understand their function and use in the cake batter. The next section will examine various mixing techniques for forming a batter.

Mixing methods

Overview

Accurate measuring of the ingredients will help to guarantee a quality product. In the home, the use of accurate measuring utensils and techniques will ensure an acceptable product. On a larger scale, weighing of the ingredients is a more accurate way to prevent any mishaps in the cake formula.

There are two types of cakes: shortened cakes and foam-style cakes. Shortened-style cakes are the most commonly prepared cakes, especially for birthday and wedding celebrations. They are made traditionally by the conventional (creaming) method or the one-bowl method. Other methods can be used, and will be discussed below. Unshortened-style (or foam-style) cakes rely on foam formation for their structure and leavening, making their preparation a challenge to the baker. The preparation of angel food, sponge, genoise, and chiffon cakes will be discussed below.

The presence and dispersion of the air bubbles is essential and can be regarded as the nucleus for the expansion of the cake. The complete dispersion of the ingredients is also a fundamental requirement for a good cake. Therefore, the purpose of batter mixing is (1) to disperse all the ingredients as efficiently as possible, and (2) to incorporate air into the mix. The incorporation of air takes place during (1) a period of rapid incorporation in the form of large bubbles, and (2) a stabilizing period when the bubbles are reduced in size (Bennion and Bamford 1973b).

There are a variety of methods used in cake making. The common requirement for all these methods is the dispersion of ingredients and the incorporation and retention of air.

Mixing methods for shortening-style cakes

Creaming method ("sugar batter" method)

The creaming method initially combines the shortening with the granulated sugar at slow to medium mixing speed until the components are thoroughly blended and the mixture has become aerated. This stage is followed by the incorporation of the eggs, while the creaming action is continued. Mixing is completed with the addition of milk and flour in alternate small portions (Pyler 1988b).

Among the major advantages of the creaming method are the incorporation of large volumes of air in the form of minuscule cells in the fat phase of the batter; the coating by the fat of the flour and sugar, which delays their respective hydration and solubilization; and the near absence of flour gluten development. In the case of the modern flours with their bleaching and low protein content, the last benefit no longer has its former significance.

Mixing time is important. Overmixing will cause a loss of air and a heavy cake. Total mixing time for the creaming method will range from 15 to 20 minutes: the initial creaming stage takes 8–10 minutes; the second stage with the incorporation of the egg, 5–6 minutes; and the final stage of milk and flour addition, 5–6 minutes. If the milk is added too quickly it will cause curdling of the batter and inversion of the emulsion to a water-in-oil emulsion.

Flour batter method

In the flour batter method, the shortening and flour are creamed to a fluffy mass in one bowl while the eggs and sugar are simultaneously whipped at medium speed to a semifirm foam in a second bowl. The sugar-egg foam is then combined with the flour-shortening mixture, after which the milk is added gradually in small amounts.

This method achieves a thorough dispersion of the shortening throughout the batter and produces an extremely fine grain and uniform texture. Higher levels of sugar and liquid are possible than with the creaming method. However, less air is incorporated, resulting in lower cake volume and pronounced development of gluten. In addition, two mixing bowls are required.

Single-stage method

In the single-stage method, all the major ingredients are introduced into the mixing bowl at one time and incorporated into a homogenous mass. Using a flat beater, the ingredients are blended together into a homogenous mixture at low speed for 1–3 minutes, followed by mixing at medium speed for 3–5 minutes, and finally again at low speed for 2 minutes, for a total mixing time of 8–10 minutes.

Emulsion method

This method is especially suited for large volume cake mixers. The sugar and shortening are creamed together for 2–3 minutes into a smooth mass. The milk is then added in several portions, with beating continued at medium speed for about 5 minutes until a light and fluffy mass is obtained that resembles a butter cream. This is followed by the addition of fl our over 2 minutes, the subsequent addition of the eggs, and mixing for an additional 4–5 minutes. The total mixing period of this method thus extends over 12–15 minutes.

Continuous batter mixing

See Industrial Preparation and Baking of Cakes: Mixing and Delivery of Batters, below.

Mixing methods for foam-style cakes

Foam-style cakes depend on eggs for their structure and volume. This is dependent on the egg's ability to occlude air and to form stable foams. Typically, as the egg white is beaten or whipped, air is incorporated, and the air cells become increasingly smaller as beating is continued. In addition, as beating continues the foam loses its sheen and reaches its maximum volume and stiffness.

Angel food cakes, which will be discussed in the next section, deal solely with egg whites; while other foam cakes (sponge, chiffon, genoise) utilize the whole egg, egg yolk and egg white separately. The yolk contains a high level of lipids that are present in an emulsified state. The additional presence of protein and lecithin endows the yolk with unusual extensibility that is conducive to foam formation. When whole eggs are beaten, air is occluded in the form of minute cells that are surrounded by films of yolk substance. The size of the bowl used for beating the whole egg is dependent on the amount of eggs. The bowl should not be too wide to allow the egg to be spread out too much. If this occurs incorporation of air will not be efficient. Also, as in the case of egg white, the rate of foam

formation and foam stability are affected by the temperature of the eggs, which should be in the range of 75–85 °F (24–27 °C); the time and level of sugar addition, with the sugar addition to egg ratio not exceeding 1.25:1; the yolk solids concentration; and the inherent quality of the eggs (Pyler 1988b).

Angel food cake

Angel food cake is a "true" foam-style cake. This means that the cake is leavened only by air and steam, with no chemical leavening. The air and steam are primarily derived from the egg whites, which with sugar constitute the main ingredients of the cake. Sugar is the tenderizing agent for the cake since the cake does not contain shortening. The major proportion of egg whites to sugar is 42:42, while flour is 15%. Cake flour plays a secondary role.

Care of the egg whites is important for a successful cake. The eggs should be separated when cold and allowed to warm to room temperature. There should be no trace of egg yolk (fat) in the white since the presence of fat will hinder the whites from beating. In addition, the bowl, beaters, and tube pan must be also grease free.

In commercial practice, the general procedure in preparing angel food cake is to first whip the egg whites, to which salt and cream of tartar have been added. Cream of tartar is considered an acid and a whipping aid for the egg white foam. In addition, cream of tartar helps to improve the color of the cake, produces a fine-grained cake, stabilizes the foam sufficiently so it will not collapse in the oven before the temperature of coagulation is reached, and prevents the drastic shrinkage of the foam during the last stage of baking and during subsequent cooling (Bennion and Scheule 2004).

Once the egg white foam starts to form soft peaks, 50–60% of the sugar (of fine crystallinity to promote rapid solution) is added in a slow stream while whipping is continued, until the meringue retains a stiff peak. The flavor materials are then added, followed by the remainder of the sugar and the cake flour that have been sifted together. Careful addition of the flour/sugar mixture is imperative. The lowest speed on the mixer is used, or the mixture is "folded in" by hand. In the process of "folding in," a rubber spatula is used to cut down vertically through the two mixtures, across the bottom of the bowl and up the nearest side. The bowl is rotated a quarter turn with each series of strokes. The down-across-up-and -over-motion gently turns the mixtures over on top of each other, combining them in the process.

The browning of the crust is not as dark as with other cakes. The Maillard browning reaction is not as intense due to the acidic pH of the batter caused by the cream of tartar. The color of the crust is characterized as "macaroon" in color.

Angel food cakes are usually baked at a high temperature (375–400 °F [191–204 °C]). Also, the majority of angel food cakes are baked in tube-style cake pans that provide a more efficient heat distribution within the batter, as well as an additional internal temperature that promotes cake volume expansion.

Sponge cake

The making of sponge cake batters may be carried out in a variety of ways. In some instances, bakers prefer to separate the whites and yolks of the eggs and beat them separately with the portion of the sugar to the desired specific gravity before recombining them; the aim of this approach is to attain the maximum batter volume. Another procedure, however, is to beat the

whole eggs, which have been tempered to a temperature of about 80 °F (27 °C) with a wire whip or blade beater at medium speed (**NOTE**: The size of the bowl is important. Example: if three whole eggs are used, then use a 1-quart bowl for beating so that the eggs are confined to a smaller area and will incorporate more air). Sugar is added at the onset of mixing or in a slow stream during beating. After the egg foam has achieved the proper volume, flour and liquid are folded in as lightly as possible to avoid breakdown of the foam. If shortening or butter is to be added, it is first melted and then folded in at the end to minimize the loss of volume. This procedure is desirable when preparing a small recipe.

In the egg-separated method, the egg yolks are beaten. The sugar, salt, flavoring, and water are added, and the whole mass is beaten until very stiff. The flour is folded lightly into the mixture, after which the stiffy beaten egg whites (stiff, but shiny and not dry looking) are folded in (Briant and Williams 1956).

Chiffon cake

Chiffon cake is a cross between a foam-style cake and a shortened cake. It has beaten egg whites to help with the leavening along with chemical leavening. It also contains liquid oil in the formula.

The egg whites are beaten in a separate bowl until stiff but not dry. In another bowl the cake flour, salt, baking powder, and sugar are sifted together; the water, oil, egg yolks, and flavoring are added; and all the ingredients are beaten together. This mixture is folded into the egg white foam.

Chiffon cakes are baked in an ungreased tube pan and are tested done when the cake springs back when touched with a finger. These cakes are cooled upside down just like angel food and sponge cake.

Genoise cake

This rich, light cake is made with cake flour, sugar, eggs, butter, and flavoring. It is similar in texture to a moist sponge cake. Since the genoise cake contains clarified butter, it can be considered a relative to the chiffon cake. Clarified butter is known as drawn butter. This butter has been slowly melted, thereby evaporating most of the water and separating most of the milk solids (which sink to the bottom of the pan) from the golden liquid on the surface. After any foam is skimmed off the top, the clear (clarified) butter is poured or skimmed off the milky residue and used in cooking.

Preparation of the genoise batter is similar to the whole egg sponge method. Traditionally, the eggs are placed in a bowl and tempered over simmering water until a temperature of 80 °F (27 °C) is reached. Then the eggs are whisked or beaten with a mixer until light and fluffy (triples in size). Sugar is beaten in gradually along with the flavoring. Cake flour is sifted prior to addition to the batter and then folded gradually into the mixture.

Approximately, ½ cup of the batter is added to the clarified butter and mixed lightly but thoroughly, and then this mixture is folded into the batter. In an alternate method, the clarified butter alone is folded into the batter. Either way, this step must be done swiftly but gently, because the fat could deflate the batter and air would be lost, resulting in a heavy product. The genoise is an extremely versatile cake that is used for many elegant desserts: petite fours, cake rolls, baked Alaska.

Baking

Cake pans

Cake pans are available in a variety of shapes and forms, ranging from fl at sheet pans to cupcake molds to form pans of various configurations. Pans for larger product sizes are generally fabricated as individual units, whereas pans for snack cake items are normally strapped into sets or consist of frames containing rows of individual cups or molds.

The weight, or gauge, of the pan's metal also affects quality: the heavier the pan the better. Crumb formation is partially dependent on the degree of heating that occurs when the cake batter is first placed in the oven, and rapid heat absorption plays a role in this. On the other hand, shiny surfaces reflect heat, which causes the cake to take longer to bake and results in a coarser grain and lower volume (Brown 2000b).

The pans are prepared prior to mixing the batter. For a shortened-style cake, the bottom is greased, but the sides generally are not. The ungreased sides provide traction, allowing the rising mixture to reach full volume. When greasing the bottom of the pan, waxed or parchment paper may also be placed in the bottom before greasing to allow for easier cake removal.

For angel food cake and sponge cake baked in a tube pan, the pan is left ungreased to allow the cake to rise. If the pan is greased the batter will not be able to grip the sides of the pan; the batter will "slip," the cake will not rise at all, and the final product will collapse and be heavy.

Testing for doneness

Once a shortened cake is done baking, it should be removed from the oven, or it will dry out. There are many methods to determine if the cake is done. When cakes are nearing doneness, they start to "wrinkle" at the pan edges. They should be removed before a gap is formed between the pan and the cake. Also, when testing for doneness in the shortened-style cake, a tester inserted into the cake comes out clean. Another method or testing for doneness is to press the top of the cake lightly with the finger. If it springs back, it is done. This method is also used for foam-style cakes.

Once the shortened-style cake is baked, it is removed from the oven and allowed to cool in the pan for 10 minutes. The cake is very fragile at this time, and due to the steam produced solidification is necessary. Allow 10 minutes for the cake to cool and then remove it from the pan and place it on a cooling rack. The rack allows even air circulation and prevents condensation and sogginess.

When the foam-style cake has completed baking, it is removed from the oven and cooled upside down. This "free standing" prevents the cake from collapsing on itself, and as it cools, the structure becomes firmer.

High altitude adjustments

Cake ingredients must be modified at altitudes higher than 3000 feet. The lower atmospheric pressure at higher elevations reduces the need for baking powder or baking soda. Also, at higher altitudes, water evaporates more quickly, and the concentration of sugar increases. Structural strength can be improved by:

- Adding 1 to 2 tablespoons of cake flour,
- Increasing the amount of liquid, or
- Reducing baking powder and/or baking soda and sugar quantities.

Increasing the baking temperature 10–15 °F (6–8 °C) increases the rate at which the cake sets by speeding the coagulation of the protein and the gelatinization of the starch.

Troubleshooting problems for proper evaluation of the finished baked product

A well-prepared butter cake is moist and fine grained, with an even crumb, a tender texture, optimum volume, and a lightly browned delicate crust (Purdy 1989). The same holds true for the foam-style cake.

The basic rules for any type of cake are to follow the method as outlined in the procedure. There should be careful preparation of all ingredients prior to mixing, especially with regard to temperature and to fruit, if being used. Prepare the cake pan if necessary, depending on the cake type. Careful handling of the batter during scaling and depositing should be observed. Scrapings from the bowl should, if possible, be kept for the next batter, but if it is necessary to use them, they must be mixed into the batter. Otherwise, if placed on top they show up in the crumb of the cake as dark streaks. Bake cakes in the preheated oven as soon as the batter is placed in the pan. If the batter is allowed to stand a long time prior to baking, air will be lost from the batter. This is especially important for the foam-style cake, in which air and steam are the principal leavening agents. The shortened-style cake contains a chemical leavening agent, and if there should be a delay prior to baking, cover the batter and refrigerate. This will slow down the reaction and decrease loss of CO_2, which is needed for volume.

Industrial preparation and baking of cakes

The general rule is that the cake should be baked in as hot an oven as possible consistent with the nature of the ingredients and the size and shape of the product. A lean mix containing few enriching agents should be baked at a much higher temperature than a mix very rich in fats, sugars, fruits, and syrups. A batter mix of the genoise type spread on a baking sheet will bake much quicker than the same mix in a cake frame (pan) that is probably three times as thick, and therefore, the baking temperature should be higher.

As the temperature rises during baking the batter thins, and some coalescence of the bubbles, with some loss of gas, occurs. The rate of coalescence depends on the bubble size and, more important, the variation in bubble size. Fine bubbles of even size impart stability to the mix and produce a fine-textured cake. Variations in bubble size and the presence of large bubbles results in an unstable mix, producing cakes of coarse and uneven texture. The process of coalescence is finally arrested by a thickening of the batter due to the swelling of the starch and the coagulation of the egg and flour proteins.

Too hot an oven will cause high crust color, small volume, peaked tops, close or irregular crumb, and probably all the faults due to underbaking. Too cold an oven will cause poor crust color, large volume, and often, weak crumb that will be very dry when eaten. Good moist eating cake is produced when the temperature and time of baking are correct. All this may seem obvious, but apart from important economic factors such as excessive moisture loss and higher baking costs, cakes and pastries are often spoiled by being baked at too low a temperature for too long a time.

Heat transfer in the oven

Whether a gas or electric oven is used in baking a cake, heat is produced. This heat energy is transferred to the food through conduction, convection, or radiation. Except for some special circumstances, all of the transfers methods listed above are employed when using a conventional oven.

The conventional oven relies on hot air for heating food, primarily by convection, but conduction and radiation can occur. Baked goods rely on freely moving currents for the transfer of heat, so it is important to ensure that baking pans are placed on racks in such a way to allow for the efficient flow of air currents. The position of the rack in the conventional oven is important for promoting an even cooking and browning of the cake. For layer cake pans the rack should be in the middle or the lower third of the oven, while for a tube pan the rack should be in the lowest position so that the top of the pan is centered in the middle of the oven for even browning.

In the convection oven, a fan circulates hot air. Therefore, baking is accomplished more quickly. Usually, the position of the rack is not an issue since there is an even distribution of the heat during baking and no hot or cold spot should exist, depending on the quality and make of the oven. Since the convection oven is a more efficient way to cook food, the temperature is lowered by 25 °F (−4 °C) from what the recipe suggests. Also, cooking time is less (as much as 25% less) than it would be in the conventional oven, even with the 25 °F reduction (Middleton 2000).

Mixing and delivery of batter

Less energy is needed in the efficient mixing of cake batters. The type of mixer used must enfold air in the batter and subdivide the air into small bubbles.

Generally, the same type of mixer can be used for both the shortened and foam-style cakes. The only factor that would be different would be the agitation that would be needed for the incorporation of the ingredients, and this is accomplished by using specialized agitators and different speeds. Both batch and continuous mixers can be used for nearly all types of cake batters.

Batch mixers

Vertical dough mixers, a class identified by the perpendicular orientation of the mixer shaft, are used widely in the food industry. A feature common to most vertical mixers is the use of removable bowls. Their other characteristics may be quite diverse–there may be one or more beater shafts, the beater shafts may move in a planetary action or remain stationary, and the design of the agitators may be varied over a wide range. The types of vertical mixers of chief interest are (1) the planetary mixers that are capable of preparing most batters and some doughs and are often used for adjuncts such as icings, and (2) the spindle mixers commonly found in cookie and cracker factories (Matz 1992b).

Vertical planetary mixers with removable bowls are used universally for the batch mixing of all types of cake batters. The agitator action is described as "planetary" because the beater has two types of movement: it revolves on its vertical axis at a relatively high speed while the axis is being moved around the inside of the bowl at a relatively slow speed. The latter, or planetary action, is in the opposite direction of the agitator rotation. The combination of motions is very effective in stirring all the ingredients and reducing dead spots.

The bowl for the mixer may be obtained in sizes of 20, 40, 80, 120, 140, 160, and 340 quarts. Even smaller sizes are available for home kitchens, bakeries, laboratories, and so on. Using the usual two-stage addition for layer cake batters, a 340-quart mixer can complete four 400- to 550-pound batches in an hour. The amount per batch depends largely on the specific volume reached. Whipped-type cakes prepared with wire whips (sponge, chiffon, angel food) require smaller batches (Matz 1992b).

A convenient feature of most planetary mixers is the easy removal and replacement of the agitator element. A large selection of agitators is available, making this machine the most versatile of all mixers in terms of mixing action. The most commonly used mixer elements are probably the dough hook, the wire whip, and the batter beater. The wire whip is an assembly of wires, wide at the top and coming to a rounded point at the bottom, designed to provide maximum air incorporation and bubble dividing action. Batter beaters used for shortening-type cakes are of either the two-wing or the less common four-wing design. The outer edges of the wings are shaped to match the curvatures of the bowl side wall and may have a white rubber insert along their edges for wiping the inside of the bowl.

Wilkenson (1987) points out that there are some types of cakes best made by batch mixing, in spite of the advances in continuous mixing technology. Some problems that he lists for planetary mixers include: (1) the scaling of ingredients is not consistently accurate, (2) mixing speeds cannot be controlled accurately, (3) the design of the mixing bowl leaves some

ingredients not mixed thoroughly, and (4) sanitation and cleanup are constant problems.

Continuous mixers

Semicontinuous mixing of cake batters was introduced in the United States in the mid-1940s. One of the first commercial continuous cake mixing systems was designed around a rotator scraped-surface mixer based on an ice cream freezer machine. Another early system used a modified Oakes marshmallow mixer. In both plants, the mixer operated continuously but was fed with a premix prepared batchwise in a standard batter mixer. About 1950, a truly continuous cake mixing plant based on the Oakes mixer was designed and installed. Since then, other manufacturers have introduced similar mixers.

The Votator mixer consists of one or more horizontal stainless steel cylinders containing axially mounted beater bars that can be set to scrape the inner wall of the cylinder. An outer cylinder is placed concentrically with the mixer tube so that a heat transfer fluid can be circulated through the annular space to heat or cool the batter as it is being mixed. Mixing action is intense, and the machine has the advantage of being operable under relatively high pressures.

The Oakes mixer has a stainless steel mixing chamber consisting of front and back stator halves, round in shape, and a circular rotor mounted between them. Concentric teeth on both inwardly facing stator surfaces mesh with teeth on the rotor. Premix batter is pumped in at the center of the back stator and is repeatedly sheared as it is forced out around the rotor and from back to the center of the front stator, where it exits. Rotor speed is continuously variable over a wide range. Only about 3 quarts of batter are present in the chamber of the largest mixer at any one time, so that dwell time is very short and power requirements are low.

Air or other gases may be injected into the mixer with the other ingredients and distributed uniformly throughout the mass as very small bubbles. The stators are jacketed, allowing coolants to be circulated. Machines with capacities up to 6000 lb/h have been offered.

The AMF mixer is similar in external appearance to the Oakes, but the mixer head is considerably different. Instead of splitting axially for dismantling, the stator separates radially. The rotor has several rows of teeth on its periphery; these mesh with rows of teeth on the inside of the stator wall. Rotor speed is continuously variable. These mixers are equipped with a batter metering pump, an air meter, and speed controls (Matz 1992b).

The Goodway mixer/foamer has a slightly conical mixing chamber, pyramidal teeth, thermal jackets, and a working pressure of 150 psi. The Fedco mixer has a cylindrical chamber several inches long with hundreds of square-tipped teeth; it encloses a cylindrical rotor having many teeth on its periphery. Flow of product is straight through the annular space. The intense shear applied to the batter in the mixing heads of this design is sufficient to emulsify air and shortening in a complete formula blend. Conventional batch mixers often require that the water be kept back until the shortening has been creamed with some of the dry ingredients. Their principal advantage, however, lies in the continuous mixer's unique ability to produce highly aerated batters such as angel cake batter from a rough premix. Air or inert gas is metered into the mixer head at a calculated rate (Matz 1992b).

Continuous batter mixers can be incorporated into completely continuous systems if production schedules warrant, as in plants making only a few varieties, and these in long

unbroken runs. In such plants, liquid ingredients and plasticized shortening are premixed in vertical tanks equipped with high-speed propeller agitators. The resultant emulsion is metered into an open vortex-type premixer to which flour is fed by a gravimetric feeder. The premixer forms a slurry that is metered into the continuous mixer along with a stream of air.

Cake batter is much easier than bread dough to transfer through pumps, pipes, valves, and meters so that the engineering for continuous production is easier for a cake plant than for a bread bakery. The economics of cake manufacture is such that expenditure of a large amount of money for continuous mixing equipment may not be warranted, however, particularly for small to medium size plants handling a large number of different formulas (Matz 1992b).

Particulate ingredients such as nut pieces, chocolate chips, and raisins cause severe difficulties in continuous mix systems. The usual solution is to bypass the continuous mixer and feed particles into the tube leading to the depositor at a rate consistent with formula requirements.

Depositing the batter

Cakes and other products made out of fluid batters assume the contours of the containers in which they are baked, so the forming or shaping machinery may be regarded as the pans themselves, and the pipes, pumps, and metering devices that deliver batter to the pans. Finishing equipment that enrobes, deposits, injects, spreads, or otherwise adds fillings, toppings, and so on, has very important effects on the appearance, cost, and nutrition of the final products.

Batter depositors may be either manifold or volumetric hopper types. Accuracy is a prime consideration. Ability to handle batters containing pieces such as raisins, nuts, and chocolate chips without reducing their size is important. The depositor should not markedly change the specific gravity established at the mixer. Whether deposited on the oven band or in open pans, the top surface of these cakes will be flat or slightly domed.

When using a fancy pan (Easter egg, bunny, etc.) the chief difficulty encountered is getting the batter to fill the cracks and crevices so that the finer details of the pattern can be seen. Sometimes the viscosity of the batter is adjusted to allow flow into all parts of the pan. Vibrating the pan strongly during and after depositing the batter is of considerable help, but it may also bring all the gas bubbles to the surface, with unfortunate effects on the appearance of the cake.

Lining fancy pans with Teflon or some other nonstick coating improves detail and reduces the possibility that some critical part of the design will remain in the pan when the cake is removed.

Baking—ovens

Band ovens

The characteristic feature of the band ovens is the continuous steel belt that forms the baking surface and which turns around two large metal drums, one at each end of the oven. There are many advantages to this. The baking chamber can be made very long (300 feet is a fairly common length), leading to fast transit times and high production rates. The band can be

extended beyond the oven entrance sufficiently to accommodate certain forming operations or it can be extended past the exit to allow a modest amount of cooling and some additional drying so that the product does not have to be removed from the belt until it is set, thus providing support for the piece during the whole period of its maximum fragility. There is no need for elaborate transfer mechanisms. The baking chamber itself can be restricted in volume to almost the minimum theoretical space required to hold the product and the hearth so that heat control is simplified and heat loss is reduced.

Baking cakes as a continuous ribbon on an oven band has become common in large installations. Individual cakes are formed by cutting pieces from the baked strip and combining them in several ways. In manufacturing cakes, batter is prepared in a continuous mixer and pumped to a manifold, or batter distributor, positioned above the band oven. The manifold spreads the batter to a uniform depth, although more than one strip may be placed on the band if baked edges are preferred over cut edges, as they may be when preparing Swiss rolls (Freihofer 1985).

In addition to restricting the shape of the finished products, baking cakes on a band also establishes limits on formulation. It is important that the batter not spread significantly during baking. Sponge cake batters of high specific gravity are preferred. The finished cakes are often lower in moisture than is considered satisfactory for conventional cakes.

Tunnel ovens

Tunnel ovens are the most commonly used oven type in the cake baking industry because they meet the baker's major concerns: minimization of energy consumption and an increase in mass production (Baik et al. 2000). Compared with the batch oven, a predominant characteristic of tunnel-type ovens is that the whole baking chamber is divided into several zones along the oven length. In each zone, the temperature of the upper and lower baking chambers can be independently controlled, so the application of a temperature sequence is possible. This gives the baker more flexibility in adjusting conditions to the optimum values for a given product. However, baking phenomena in tunnel ovens are more difficult to predict than those in batch-type ovens, which usually operate at a constant temperature. The baking chambers of tunnel-type multizone ovens exhibit wavy temperature profiles along their length (Baik et al. 2000).

Impingement technology has been used in many areas, including manufacture of metal, glass, plastic, and tiles but one of the most successful applications has been in the baking industry. Impingement ovens became well known in the food service industry in the 1970s, and their use in baking expanded in the 1990s. Impingement (which directs hot air jets at baking items) improves oven efficiency and accelerates baking, thus achieving the desired changes with more rapid convective heat transfer. The advantages of impingement ovens include reductions in baking times and lower baking temperatures, the main process factors contributing to end-product moisture content and shelf life. The baking time reduction also depends on product composition and thickness. Impingement technology has been used for wide, fl at products (e.g., pizza, tortillas, pie crusts, and sheeted dough) and for small finger-size products (Dogan and Walker 1999).

How would cookies, cakes, and breads be produced in such an oven? Li and Walker (1996) conducted research on baking cakes in three types of air impingement ovens (two were commercial conveyor types; the other was a wind shear jet sweep variable speed laboratory

model), a hybrid (microwave/ air impingement) oven, and a reel oven. Li and Walker (1996) found that when cakes were baked in the air impingement ovens, baking time was reduced by almost half but produced cakes very similar to those produced in the control (natural convection reel-type) oven. Incorporating an impingement oven with a microwave into the study enabled a further reduction of baking time to one-fourth. Baking efficiency and rate have been improved with the development of combination microwave/impingement ovens, in which products can be baked more evenly and browned (Walker and Li 1993). Cakes baked with microwaves had similar color, but 15% less volume and firmer texture than the control cakes.

Reel ovens

The baking chamber of a reel oven (also called a revolving tray oven) is somewhat of a cubic compartment with varied widths, depths, and heights. This insulated enclosure has a door in front almost the width of the oven, but usually less than a foot high. Inside the chamber is a Ferris wheel-type mechanism that moves four to eight shelves in a circle centered on the sides of the oven, so that each shelf is brought past the door during every rotation. An indicator on the front of the oven identifies the shelf that is passing the door at any given time, so that the operator can stop rotation and add pans to, or remove them from, specific shelves. Ovens specialized in size and other construction features for cookies, rolls, pies, and other products are available.

Reel ovens can be heated by gas, electricity, or oil. With gas or electricity, the heating elements are placed on the floor of the oven. Gas ovens usually have a baffl e placed above the burner to change part of the flame's energy to radiant heat. To apply steam, perforated steam sprayers that are effective in the entire chamber or in a partitioned zone can be installed.

There are side-to-side and top-to-bottom variations in temperature. The vertical differences are canceled out for all practical purposes by the reel's rotation, but the horizontal differences are not, and bakers often find there is a significant variation in the baking response of doughs placed on the left side from those placed on the right side of the shelf. Some fluctuations of temperature occur when the door is opened. In spite of these negative features, the reel oven has been found to be satisfactory for baking many types of products.

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Biscuits

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Introduction

Bakery products form an important part of the diet worldwide. They are eaten as breakfast food, snacks, and as a staple product in the form of bread. Biscuits are the most popular bakery items consumed by nearly everyone. This is mainly due to their ready-to-eat nature, good nutritional quality, availability in numerous varieties, and affordability. Based on production statistics, the top three producers of biscuits are the United States, China, and India, respectively. The wide variety of types that are possible is a major attraction of biscuits, which are nutritious convenience foods with a long shelf-life.

The word biscuit is derived from the Latin word *panis biscotis* meaning twice cooked bread (Sharma and Zhou 2011). This is because the original process consisted of baking the biscuits in a hot oven and then drying them in a cool oven. Biscuit has two meanings: (i) small round bread leavened with baking powder or soda; (ii) any of various small flat sweet cakes. "Biscuits" is the original British word used to include small baked products (usually flat) based on wheat flour with various inclusions of fat, sugar, and other ingredients. The name "biscuit" is synonymous with "cookie" but the former is more comprehensive in meaning in the United Kingdom and the Indian sub-continent and the latter in the United States. Wafer biscuits represent a special type of baked product because they are formed between a pair of hot plates and not on a baking band or wire as are most other types. Today, biscuits are a part of snacks, luxury gifts, dietary products, infant foods, and also come with the addition of many expensive ingredients, such as chocolate and cream. In general, biscuits are recognized as cereal based products that are baked to a moisture content of less than 5%. The cereal component is variously enriched with two major ingredients – fat and sugar (Manley 1983).

Classification of biscuits

Based on dough characteristics, biscuits are classified into:

- short or soft dough biscuit
- hard dough
- crackers (fermented or non-fermented).

Depending on the method of production, soft dough biscuits are further classified as rotary molded or wire cut. The difference in the viscoelastic properties of soft and hard dough is mainly due to the variation in the level of sugar and fat as well as mixing conditions. Hard dough normally contains a lower level of fat and/or sugar, while short dough contains a higher amount of fat and sugar. Biscuits are also classified on the basis of taste into three categories.

1. Sweet biscuits – produced mainly from soft or short dough's and with a high water and fat content.
2. Semi-sweet biscuits – also known as tea biscuits. They are produced from hard dough and are characterized with having low fat and sugar.
3. Salt biscuits – crackers or puffed biscuits are included in this category. These biscuits are prepared from generally fermented dough or even unfermented hard dough and have a low amount of fat and sugar. However, the apparent fat is usually considered high, as these biscuits are usually layered or brushed with oil or oil sprayed.

This chapter discusses the role of individual ingredients, the manufacturing processes of biscuits, and aspects of their quality. An update on recent developments in healthy biscuit formulation has also been provided. Crackers and fermented biscuits have not been discussed, as they need a separate discussion. It is important to discuss the role of various ingredients to better understand the biscuit baking process.

Ingredients in biscuit and their role

The principal ingredients used in the manufacture of biscuits are wheat flour, fat, and sugar. The quality of biscuit is governed by the nature and quantity of the ingredients used. Several researchers have attempted to describe the effect of ingredients in a dough and formula balance on the final structure of the product, and have reported the correlation between the characteristics of the raw materials – specifically flour – and the quality of the product (Saha and others 2011).

Wheat flour

Flour is a very important and basic constituent of biscuits. Wheat contains 85% endosperm, 13% bran, and 2% germ. For biscuit making, refined wheat flour is used which is mostly the endosperm part of wheat. The type of flour used depends on the biscuit: short dough variety – weak flour (7–9% gluten); hard dough variety – strong flour (9–11% gluten); and fermented dough variety – strong flour (9–11% gluten). Flour from different varieties of wheat varies in protein content and quality. According to De La Roche and Fowler (1975), an increase in the protein content tends to reduce the length of biscuit after baking. Unlike bread making, where the quantitative and qualitative importance of the proteins is well known, the influence of gluten on the quality of biscuit dough is difficult to define (Saha and others 2011). There are very few reports concerning the role of gluten in biscuit making. Flour used for biscuit making is usually checked for cleanliness. It should be free from extraneous matter, free flowing, and be white to creamy white. On sieving, biscuit purpose flour should pass through 24-mesh size sieve. In general, it can be said that the properties of a good biscuit flour and a good bread flour are opposites. Biscuit flours are made from low protein content, low starch damage flours, and a moderately low falling number can be helpful. It is worth mentioning that falling number results are recorded as an index of enzyme activity in a wheat or flour sample and the results are expressed in time as seconds. A preference for low protein, low starch damage flour in biscuits is obvious when the role of protein and damaged starch as water binders is considered. Also, bread flours are treated with oxidizing agents while biscuit flours are treated with reducing agents.

When mixed with water, the important proteins glutenin and gliadin contained in wheat form gluten, which is tough, rubbery, and elastic in nature. It gives structure to the biscuits and holds other ingredients such as sugar, shortenings, water, and so on. The major functions of wheat flour in biscuit dough are:

- to form the dough during mixing, holding all the ingredients uniformly distributed in the dough and making easy machinability possible;
- to retain the gas during fermentation and baking;
- to form the structure of biscuit.

Sugar

Sugar is an important ingredient of short-dough biscuits. The sugar used in biscuit baking can range from simple sugars such as glucose and levulose (monosaccharides) to complex sugars

such as sucrose and maltose (disaccharides). Usually sucrose (normally as a solid) and glucose syrup are used. Lactose can be present directly as an ingredient or in skimmed milk or whey powder. Maltodextrins, which are effectively low dextrose equivalence (DE) glucose spray-dried syrup, are sometimes added to enhance crispness. In brief, the sugar used in biscuit manufacturing can range from invert syrup, golden syrup, glucose syrup, honey to a high fructose product.

The quantity, granulation, and type of sugar used influence the quality of the biscuit. The amount of sugar that goes into solution depends on the particle size of the sugar, and greatly influences the spread of biscuits and machining properties of dough. From a functional viewpoint, sugar restricts the development of gluten by competing for water which otherwise would have been absorbed by the gluten (Yamazaki and Lord 1971). An obvious outcome of this is a general increase in the spread and a reduction in thickness of the biscuits (Zoulias and others 2000). Further, a slight increase in sugar content has been associated with improved dough firmness (Slade and Levine 1994). Note that the changes in dough consistency due to sugar content depend on the type of cookie dough. To cite a few examples, the consistency of wire-cut doughs remain constant at sugar levels between 300 and 450 g/kg, while a sharp increase in dough consistency can be observed in deposit cookie dough. For rotary-molded biscuit dough, only a marginal increase in dough firmness has been reported for increased sugar content (Miller 1985). The functions of sugar in biscuit making can be summarized.

- Sugar imparts sweet taste and flavor.

- It has a tenderizing action on flour proteins.

- Being hygroscopic, sugar helps to retain moisture, which improves its shelf-life.

- The color of biscuits is due to the caramelization of sugar as well as to the sugar–amine (Maillard) reaction.

- Sugar has a lubrication effect on gluten strands and helps in acquiring volume.

- Sugar is essential for the fermentation activity of yeast to produce CO_2 gas which raises the dough and imparts proper volume to the dough.

Fats, oils, and emulsifiers

Fats and oils are used in dough as surface sprays, cream fillings, and coatings. As biscuits are a long-life product, any fat used in them has to be stable under the conditions of storage. Vegetable oil, butter, and inter-esterified fat are commonly used in biscuit making. In cookie production, plastic shortening is creamed with sugar to incorporate air bubbles that are trapped in the liquid phase of the shortening. To be effective the shortening must possess "plastic" properties, which are in turn exemplified by the correct solid-to-liquid index at the dough mixing temperature (Jacob and Leelavathi 2007). Fats used in biscuit making should be high quality as they can undergo lipolysis if the fatty acids are split from the glycerol, either due to saponification (in presence of bicarbonate leavening agents), chemical oxidation or the action of enzymes. For this reason, fats and oils used in biscuit making are always added with antioxidants. These help to prevent oxidative rancidity and off-flavor development. The major functions of fats and oils in biscuit preparation are:

- to impart a tenderizing effect to the dough and hence the biscuit is soft textured;
- to improvethe machinability of the dough;
- to improve the palatability of the biscuit.

If appropriate emulsifiers are used, it is sometimes possible to reduce the fat content of a recipe by about 20%. This change could be made either for nutritional considerations or for a desire to reduce the use of the most expensive major ingredient. Utilization of emulsified bakery shortening helps in the fine dispersion of the fat in the batter or dough system (homogenous dough) as compared to non-emulsified shortenings. Glycerol monostearate (GMS), sodium stearoyllactylate (SSL), and lecithin (commercially obtained from soya) are the most commonly used emulsifiers. A blend of surfactants in semi-sweet biscuits has been associated with several advantages, such as increased mixing time, greater mixing stability, reduced rate of dough breakdown, uniform fat distribution, prevention of moisture migration, and improvement in texture (Mahdi and Dawoud 1986). GMS improves the ability of protein film to entrap air in the batter during creaming or mixing. Thus biscuits open out more during baking. Entrapped air gives porous texture and crispiness to biscuits, in addition to improving palatability. Cookie dough containing SSL or sodium stearoylfumarate has been shown to exhibit a marked increase in spread (Tsen and others 1973; Manohar and Rao 1999a).

Water

Water plays an important role in biscuit making. Water is required at the dough mixing stage, but should more properly be regarded as a processing aid rather than an ingredient because the added water, together with that present in the flour (about 14% by weight, wet basis) and other ingredients, such as sugar syrups, is largely removed during the baking process. The limited amount of water used in biscuit formulation, and also its non-availability to protein and starch, partially contributes to the crispness of biscuits.

Water functions:
- to help form gluten, starch-swelling processes, and to bring dough ingredients in intimate contact;
- to assist in control of dough temperature;
- to make enzyme activity possible;
- to help to a certain extent in biscuit aeration by the formation of steam;
- to help dissolve salt, chemicals, water soluble color, and flavor and to distribute dissolved materials throughout the dough.

The initial moisture level in the flour has more influence on the surface characteristics of biscuits than the total water in the dough. For a given recipe, the consistency of biscuit dough could be adjusted by varying the water content (Wade, 1988). A variation of even 1% in water content could considerably change the various rheological characteristics of biscuit dough (Manohar and Rao 1999b). To summarize, water is added during the dough stage and driven out during the baking stage. Water carries out its functions between the time of its addition and the time its removal.

Leavening agents

Leavening is process by which the dough is filled up with gas pockets, which are retained even after baking. Biscuits are usually chemically leavened, with ammonium carbonate (referred to as "vol" in baker's term) serving as the leavening agent; it is an aerating agent and does not require the addition of an acid to evolve carbon dioxide. Chemical leaveners aerate the dough, thereby rendering it light and porous and give the right gauge (thickness) and smooth texture to the biscuit. The chemical production of gases occurs when chemical leaveners break down in the presence of moisture or heat, giving off gases. They differ from other aerating agents in that almost no gas evolves in the cold, and under the influence of heat it decomposes to yield three gases: ammonia, carbon dioxide, and water vapor (steam). In conventional chemical leavening formulas, the acid component of the leavening formula reacts with sodium bicarbonate ($NaHCO_3$) (or ammonium bicarbonate, NH_4CO_3) in the presence of moisture, so the baking soda breaks down quickly and easily to carbon dioxide and water. With acid, less baking soda is needed to produce carbon dioxide for leavening, so there is less discoloration and fewer chemical off-flavors. The dry acid is usually cream of tartar ($KHC_4H_4O_6$) or sodium aluminium sulfate ($NaAl(SO_4)_2$). Both the reactions are shown here:

$$NaHCO_3 + KHC_4H_4O_6 \rightarrow KNaC_4H_4O_6 + H_2O + CO_2$$
$$3NaHCO_3 + NaAl(SO_4)_2 \rightarrow Al(OH)_3 + 2Na_2SO_4$$
$$+ 3CO_2$$
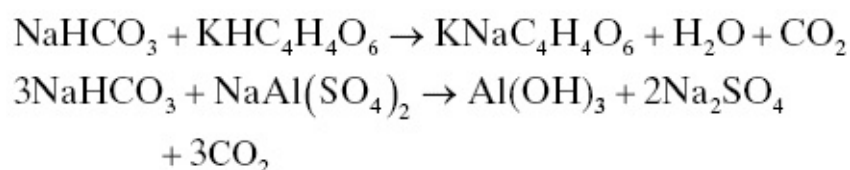
Double-acting baking powders contain two (or more) acids: one that dissolves and reacts with baking soda at room temperature; another that requires heat to dissolve and react. Other commonly used natural acid forms could be sour cream, most syrups (including molasses and honey), unsweetened chocolate, and cocoa (Figoni 2007).

Minor ingredients

The minor ingredients are listed here.

- *Salt* imparts flavor, accentuates the flavor of other ingredients, removes flatness and has strengthening effect on gluten.

- *Dairy ingredients* include dairy products such as skimmed milk powder (SMP), glucose/dextrose, and so on. The presence of proteins and amino acids from milk powder help in browning reactions, thereby imparting color to the biscuits.

- *Flavors and colors* help to impart a desirable flavor and color to the final product. In all its many forms vanilla as flavoring stands pre-eminent in the biscuit world. Addition of vanilla extract has been associated with a higher antioxidant activity and a lower peroxide value in biscuits (Anuradha and others 2010).

- *Egg solids*; egg is not a common biscuit ingredient and the use of egg solids is limited to some type of cookies mainly for their albumin content, which is responsible for aeration.

- *Acidulants* are often included at low concentrations in biscuit dough formulations to modify the dough properties. Sodium metabisulfite (SMS) is frequently included in the

recipe formulation of semi-sweet biscuit dough to minimize dough contraction following sheeting (Oliver and others 1995). SMS acts as a source of sulfur dioxide and weakens the elastic properties of the gluten, hence reducing the likelihood of dough piece shrinkage, by breaking some of the disulfide bridges present in the gluten proteins (Oliver and others 1996). Alternatives to SMS are l-cysteine hydrochloride and proteinases, which unlike SMS do not cause the destruction of vitamins during baking.

- *Gums and hydrocolloids*; hydrocolloids can be used to control the rheology and texture of food products.

Biscuit production process

The flow chart in Figure 33.1 provides a brief introductory description of the biscuit making process and the sub-processes.
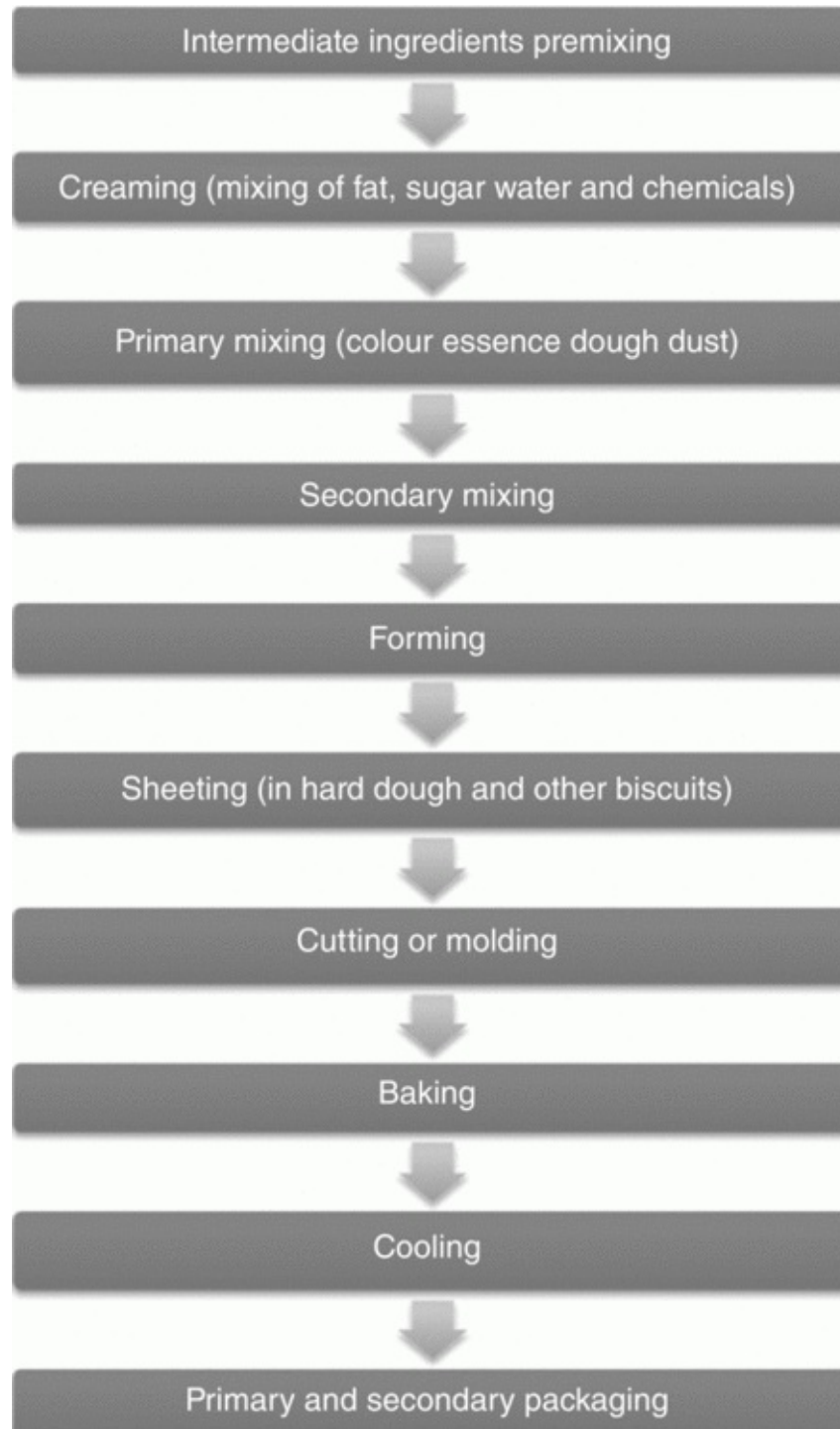
Figure 33.1 Process flow chart for manufacture of biscuit.

Biscuits are made primarily from wheat flour, sugar, fat, and leavening agent, along with other minor ingredients. These ingredients are mixed together in accordance with one of a few approaches available for mixing in dough mixers. This yields the biscuit dough, which is then worked upon using rollers to obtain sheets (sheeting process) of dough having optimal thickness. The shape of the biscuit is obtained from cutting moulds on the conveyer line, from where they enter into the baking oven. Baked biscuits are allowed to cool and are then

packaged. The process may have additional sub-steps depending on the type of biscuit and the choice of the process. This section provides an introduction to biscuit making and forms a basis for more details on the individual steps involved and described in subsequent sections.

Mixing

Introduction

The first step in the manufacture of biscuits, and in fact any baked product, is the mixing of the ingredients used in the recipe to form dough. Dough is the intermediate stage between flour and the bakery product. The dough characteristics depend on several factors such as ingredient quality and quantity, mixing conditions, resting time, and the temperature of the wheat flour dough (Bloksma and Bushuk 1988). Mixing is one of the important and critical unit operations involved in the preparation of biscuits as it influences the development of gluten, and hence the rheological properties of the dough. The rheological characteristics of the dough are very important, as they influence the machinability of the dough as well as the quality of the finished product (Manohar and Rao 1999c).Water hydrates ingredients like flour and, if conditions are right during subsequent mixing, hydrated wheat protein changes into a viscoelastic material known as gluten. The formation of gluten during mixing is very important as it decides the nature of the dough in the forming processes and ultimately the structure in the baked biscuit. It is worth remembering that the formation of gluten depends firstly on the hydration then on a period of mixing so this is both time- and energy-dependent. It would be useful to be able to adjust the dough water level before the completion of the mixing to achieve a desired consistency. The flour in short dough(s) is given very little mixing; this minimizes the development of the protein network. For short dough, slight development of gluten is necessary to enable sufficient cohesion for handling and shaping the dough (Olewnik and Kulp 1984). However, much of the cohesion in the biscuit dough that is observed on pressing it into a mould is reported to be due to the presence of plastic shortening (Hoseney 1986).

Different types of biscuits require dough of varying rheological properties to enable proper machining, as well as to obtain an end product of high quality. Continuous and batch mixers (either vertical or horizontal) are both used for dough mixing. The rheological properties of biscuit dough depend on several factors, such as mixing method, type of mixer, level and type of ingredients, and the temperature of the ingredients. Normally, to obtain short dough, the creaming method (CM) is used to minimize gluten development (Smith 1972). In cookie production plastic shortening is creamed with sugar to incorporate air bubbles that are trapped in the liquid phase of the shortening. To be effective, shortening must possess "plastic" properties which are in turn exemplified by the correct solid-to-liquid index at the dough mixing temperature (Jacob and Leelavathi 2007). Biscuits produced using the all-in-one method (AOM) are usually considered inferior to those produced by the two-stage CM (Wade 1988). Vettern (1984) has reported an increase in spread when cookies were made either by a creaming or an "all-in-one" mixing method, but the spread was greater at all sugar levels with the "all-in-one" method of mixing.

Mixers used for biscuit making can be either horizontal or vertical type mixers. Similarly, continuous and batch type mixers are both used for mixing. However, batch type mixers are popular, because the time required to mixing the dough is often less than that required for its consumption in the overall process. The design of a mixer also has a significant effect on the

quantity of energy that can be transferred to the dough for a given mixing time (Cauvain and Young 2006). Vertical type mixers are usually characterized by a higher rate of energy transfer to the dough relative to the horizontal type. Note that the transfer of energy is an integral part of developing a gluten network.

Sheeting and cutting

While mixing is common to all biscuit types, the methods of forming the individual units vary from sheeting (semi-sweet), to molding (short dough), extrusion (rout pressing), sheeting and lamination (crackers), and even depositing (wafers) (Cauvain and Young, 2006). Sheeting is the process in which sheets of nearly uniform thickness are obtained from the dough by the application of continuous compressive force. In practice, the desired thickness of the dough sheet is attained by passing the first sheet through a series of "gauge rolls" to subsequently reduce the thickness in a controlled pattern. The gauge rolls have set of cylindrical rollers which rotate in reverse direction so as to give a push to the next gauge rolls. Three to four stands of gauge rolls are used in a normal biscuit production line. For certain types of biscuits "lamination" is preferred, especially to impart a laminated structure and therefore a unique texture. This involves the machine rolling back the first sheet to pile it on top of the former, followed by subsequent reduction in thickness. Biscuit doughs contain a well-developed gluten network which, during the sheeting operation, becomes aligned in the direction of machining (Oliver and others 1996). It should also be emphasized that the efficiency of the processes can be influenced by any change in the biscuit recipe or formulation. For example, fat influences the dough machinability during processing and the dough spread after cutting (Vettern 1984; Jacob and Leelavathi 2007).

The dough sheets are then passed through cutting rollers which cut the dough into the desired shapes. The dough cutters are usually stainless steel cylinders with the desired shape forming units engraved on top of them. Molders are now designed in rings instead of single piece which helps in maintenance or changing damaged cups. Molders are used for short dough whereas cutters are used for hard dough varieties. Molding has the advantage that only one relatively simple machine is needed to convert a mass of dough into dough pieces ready for baking. There is no production of "cutter scrap" dough, which has to be recycled, but there are significant limitations in the consistencies of dough that can be handled and on dough piece weight adjustment (Manley 2001).The conveyor takes the dough (semi-finished biscuits) into the baking oven (or sprinkling unit) and the remaining scrap dough material is diverted back over a scrap return conveyor to the mixing section for reuse. After the sheeted dough is cut, the aligned gluten proteins may relax, causing a change in shape of the cut dough piece. This change in shape can cause problems in situations where the product must fit exactly into molds for coating or is to be wrapped in packets of fixed dimensions (Oliver and others 1996). For some biscuit varieties where spice, salt or sugar is sprinkled on top, this is accomplished after the cutting stage using specialized sprinkling machines.

Baking

Industrial biscuit baking takes place in tunnel ovens of varying lengths (15–100 m) and widths (0.8–1.2 m). There are two principal types of tunnel ovens: the direct-fired type where heat generation occurs within the baking chamber (generally using gas burners or electrical heating elements above and below the conveyor band), and indirectly fired ovens where heat

generation occurs in a combustion chamber separated from the baking chamber by steel walls (Broyart and Trystram 2002).

A biscuit baking line is usually divided into different zones (see Figure 33.2). In general, the number of baking zones may range from two to six with independently controlled heating systems. The typical temperatures in different zones of a tunnel type biscuit baking oven and the importance of each are presented Table 33.1. The different forms of biscuits and cookies are baked directly on the oven band and, being small thin units, they are rapidly baked at relatively high temperatures (Cauvain and Young 2007). It is worthwhile mentioning that the temperatures in different zones increase progressively as the biscuits make their way from the entrance of the oven to the exit. This is important because it prevents the rapid surface hardening of the biscuits, which prevents further escape of moisture leading to the problem of "case hardening".

Table 33.1 Example of a biscuit baking oven configuration with six temperature zones. The temperature-residence time combinations in each zone impart specific characterstics to the biscuits

Parameters	Temperature (°F)	Importance
Temperature Zone 1	410	Initial heating
Zone 2	455	Chemical reactions of ingredients
Zone 3	490	Chemical reactions of ingredients
Zone 4	520	Baking – increase in size
Zone 5	515	Coloring zone
Zone 6	510	Coloring zone
Total baking time	4 min	Quality control
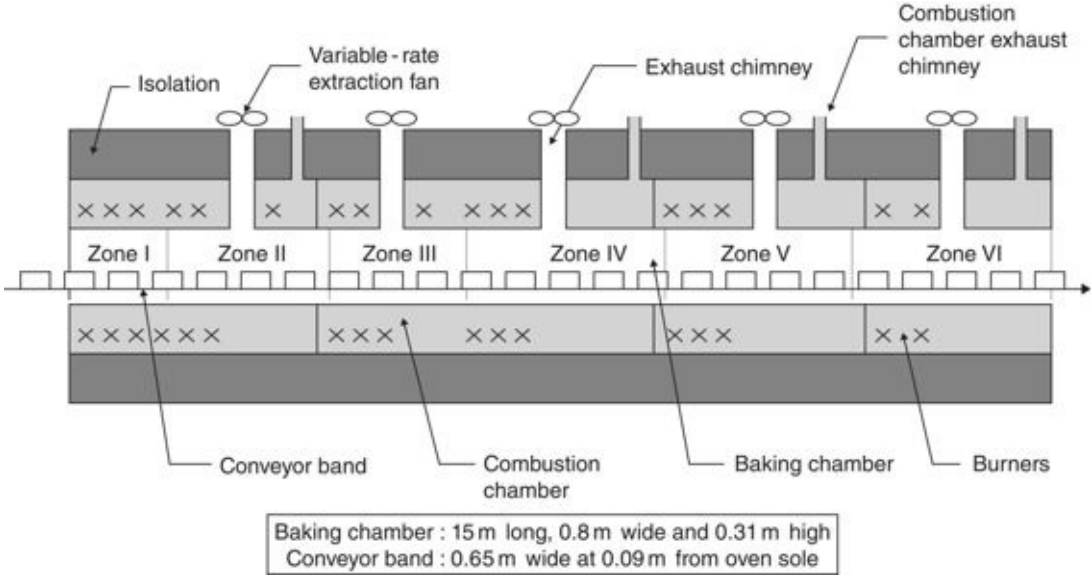
Figure 33.2 Schematic of a 15 m long, pilot-scale, indirectly fired, multiburner oven. (Adapted from Broyart and Trystram (2002). Reproduced with permission of Elsevier).

Three types of baking ovens are most prevalent at industrial-scale biscuit manufacturing: gas fired, oil fired, and electric. In any type of baking oven, the heat transfer to the product occurs

by the three main modes: conduction, convection, and radiation. Baking is a complex process involving simultaneous heat and mass (water) transport within the oven. Since radiation is the main mode of heat transfer in any biscuit oven, the role of water vapor in radiant exchanges is also significant and should not be assumed to be negligible (Broyart and Trystram 2002). The various modes of heat transfer occurring inside a biscuit baking oven are summarized in Figure 33.3, illustrating the complexity of the baking process. The mode of heat transfer to the dough and the amount of heat decide the structure of the product and the associated changes.
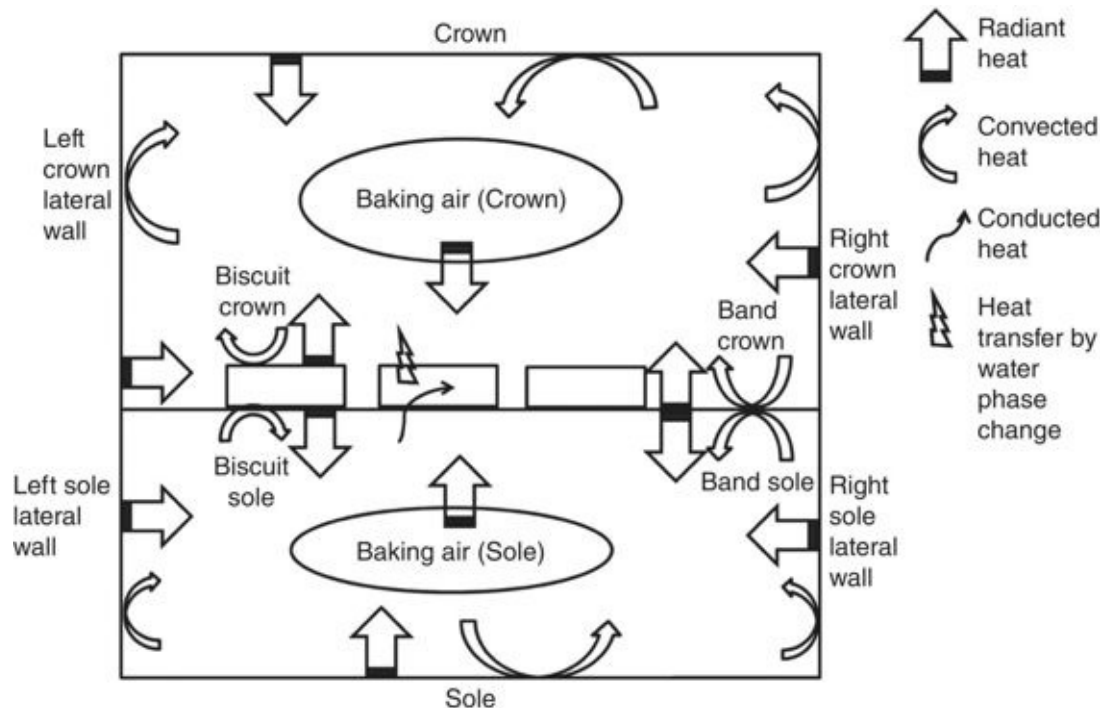
Figure 33.3 Cross-section of a biscuit baking oven and different modes of heat transfer that must be considered. (Broyart & Trystram 2002. Reproduced with permission of Elsevier).

In any type of oven, the principal control points are conveyor speed (defining baking time and production rate), the amount of heat supplied by all heating elements above and below the product, and the extraction rate of each chimney (Broyart and Trystram 2002). Baking results in several physical, chemical, and biochemical changes in the cereal matrix such as volume expansion, evaporation of water, and formation of porous structure, denaturation of proteins, starch gelatinization, crust formation, development of desirable taste, pleasant flavors, and browning. However, the two major physical changes that occur during baking of biscuits are the appearance of a brown surface color through the Maillard reaction and the considerable loss of water (Sablani and others 1998). The Maillard and caramelization chemical reactions responsible for color and flavor development depend on the type of substrate, temperature, water activity, and pH (Rufián-Henares and others 2008). Where required, the biscuits are sprayed with oil as soon as they are taken out of the oven. This improves the surface properties of the biscuits, their color, and taste.

Cooling

Stripper conveyors (wire mesh structures) are often provided at the delivery end of oven so that baked biscuits are cooled and do not come in contact with any surface when hot. Cooling conveyors are on an average twice as long as the baking line. Biscuits leaving the cooling

conveyor enter the packaging zone. The low moisture content of biscuits ensures that they are generally free from microbiological spoilage and this confers a long shelf-life on the products, provided they are protected from the uptake of moisture from damp surroundings.

Packaging

A stacking machine is used to distribute and arrange biscuits in a line, so that they can be stacked easily for the packing process. The biscuits pass through plates, which act as guides directing their fall into the space between the guides. There are various types of biscuit packing such as pile type, on the edge and cream sandwich type. Horizontal flow wrap machines are usually used to pack with flexible packaging.

Biscuits have a low moisture content, high fat level, and are fragile, so these three aspects have to be protected. Packaging plays vital role in maintaining the quality of biscuits. The shelf-life of biscuits depends on the inherent characteristics of the product, the barrier and other functional properties of the packaging material, the packaging operations adopted, the distribution and storage patterns followed, and economic considerations.

Because biscuits are moisture-sensitive products, the rate of water vapor transmission of the packaging material used is of importance as it is closely associated with drying, physical structure, and protective action against oxidation (Robertson 2006). This can be achieved either by packing the biscuits in end-fold style portion packs or by gas flushing the pillow packs, thus preventing breakage during transport and retail handling. Accordingly, primary packaging materials for most biscuits range from biaxially oriented polypropylene, polypropylene, metalized polyester, and other laminates. For secondary packaging, corrugated board boxes (made of cellulosic cardboard) are widely prevalent globally. A variety of flexible packaging materials are used for packaging biscuits, however, which have advantages such as functionality, lower cost, printability, light weight, savings in freight, and other such factors. The biscuit pack must also give mechanical protection to the product. For this reason, thermoformed plastic trays of polyestyrene or polyvinyl chloride with multiple cavities are used. They are closed with a snap-on lid or overwrapped, shrink-wrapped or sealed with a lidding material.

Problems and solutions

Several problems can and are encountered by biscuit baking industries at various stages of production. Such problems could be the outcome of a change in recipe, process or any other foreseen causes at some stage. A few of the common problems encountered during baking and their possible solutions are presented in Figure 33.4.
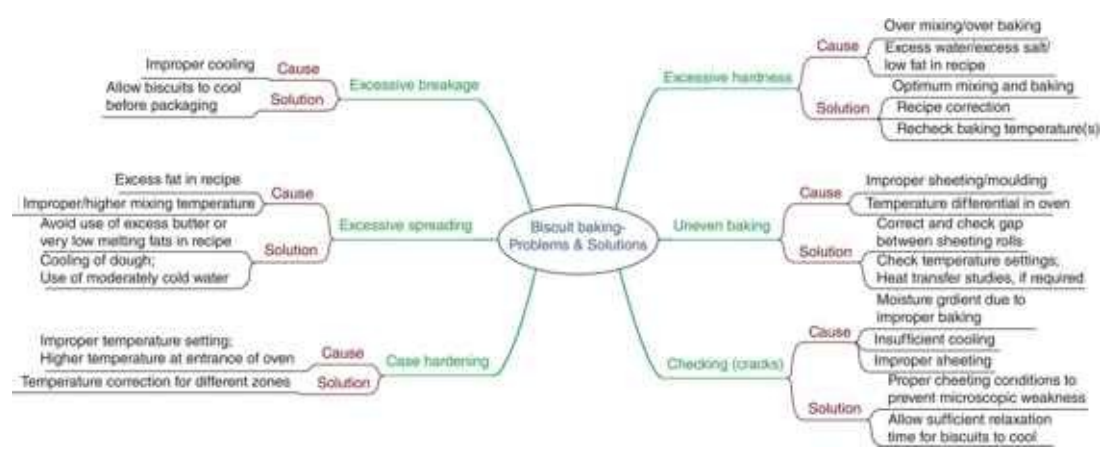
Figure 33.4 Causes and solutions for selected problems during biscuit baking.

Quality control in biscuit manufacture

Quality assurance systems take a much broader view of what is involved in satisfying consumer's needs. The quality assurance system focuses on the prevention of problems and not simply on their cure. The quality of biscuits is influenced by several factors such as the quality and level of ingredients used, and processing conditions such as mixing, molding of the dough, baking, and cooling of the biscuits. Among the ingredients, the quality of flour, sugar, and fat greatly influence the quality of biscuits. Since quality is influenced by interactions between several factors, test baking has been found to be the method of choice when predicting the suitability of flour for biscuit making (Manohar and Rao 2002).

Quality parameters for ingredients

The various physical and chemical tests performed on the raw ingredients can be summarized:

- *wheat flour* – moisture, total ash, acid insoluble ash, germ oil acidity, alcoholic acidity, gluten content, sedimentation value and rheological characteristics of the dough;

- *oils and fats* – acidity as oleic acid, iodine value, peroxide value, saponification value, qualitative test for antioxidants, free fatty acid, melting/slip point of oil, moisture, color of oil, Kries test, Bauduine test

- *crystal sugar* – moisture, reducing sugar, sieve granularity;

- *skimmed milk powder* – moisture, solubility, titrable acidity (% of lactic acid), total ash (on dry basis);

- *condensed milk* – moisture, sucrose content, acidity, fat content (Gerber method);

- *butter* – acidity, salt content;

- *leavening agents* – purity of sodium bicarbonate and ammonium bicarbonate is checked;

- *acidulants* – purity and neutralizing value (examples include acid calcium phosphate, sodium aluminium sulfate, sodium acid pyrophosphate;

- *emulsifiers* – emulsifiability, soap content, moisture, alpha monoglycerides and free glycerides.

Quality parameters for biscuits

Quality control is of major importance in the food industry. Consequently, the inspection of the biscuit bake level occupies a major role in the biscuit manufacture process as it affects the taste, texture, and appearance of the products (Yeh and others 1995). The final biscuits are routinely analyzed, usually daily, for moisture, total ash, acid insoluble ash, fat content, acidity of extracted fat, and texture.

- *Moisture content of biscuits* – The moisture content of biscuits is usually measured gravimetrically by drying in a hot air oven maintained at 105 °C. For quick and regular testing, halogen moisture meters are also common in biscuit manufacturing industries.

- *Acidity of biscuits* – The acidity of extracted fat from biscuits is one of the criteria for evaluating biscuit quality and studies have shown that in addition to major ingredients such as flour and fat, minor ingredients such as corn syrup, milk powder, and baking chemicals considerably influence the acidity of soft dough biscuits (Vatsala and Rao 1987). The acidity of extracted fat is usually expressed as percentage oleic acid.

- *Pasting properties* –The Rapid Visco Analyser (RVA) is a useful tool for studying starch pasting properties and the effects of other food ingredients on starch performance. The RVA indicates starch viscosity (by measuring the resistance of flour and water slurry to the stirring action of a paddle) (Mamat and others 2010).

- *Biscuit density* – The density of biscuits is most often determined by the solid replacement technique using rapeseed. For this, a container of known weight and volume is filled with rapeseed and excess rapeseeds are trimmed off slowly. The bottom of the container is covered with rapeseed and a biscuit of measured weight is placed in the container with the flattest surface downwards. The container is filled with rapeseed and the total weight measured. The mean of several determinations is taken as the density (Mamat and others 2010).

- *Texture of biscuits* – Texture is an important element of biscuit and cookie quality that affects consumer acceptance and repeat sales. Probe testing (also called penetrating, puncturing or punching) is one method for measuring the textural properties of biscuits. However, the three-point bend test (also called the three-beam snap technique) is a common technique used to evaluate textural quality (hardness and fracturability) of cookies (Gaines and others 1992). In each test, the peak force (hardness) and distance to peak (that is, distance to reach peak height) are measured and these two parameters are used to estimate the texture characteristics. Note that biscuit structure is a complex composite matrix of protein aggregates, lipids, and sugars embedding starch granules.

- *Biscuit color* – The color of the two surfaces of a biscuit (top and bottom), in terms of brightness (L^*), redness (a^*) and yellowness (b^*), are measured using a colorimeter, calibrated with a black glass and a white tile. The scale for a^* varies from green (negative) to red (positive) and the scale for b^* corresponds to a yellow-blue scale on which yellow is positive.

- *Biscuit dimensions and spread ratio* – The long diameter, short diameter, and thickness of the biscuits are evaluated using a vernier caliper. Spread ratio is an important physical quality parameter of biscuits, defined as the ratio of width of the biscuits to that of the thickness and expressed in percentage, for circular or round biscuits.

$$Spread\ Ratio = \frac{Width}{Thickness} \times 100$$

Spread ratio provides information about the post-baking shape characteristics and the spread of the dough.

Healthy biscuit formulations

Most bakery products are used as a source for incorporation of different nutritionally rich ingredients for their diversification. Encouraging trends in the consumption of bakery products by populations from different income groups indicatethat there is a vast scope for the nutritional enrichment of bakery products, especially for developing countries. Because of competition in the market and the increased demand for healthy, natural, and functional products, attempts are being made to improve the nutritive value and functionality of biscuits by modifying their nutritive composition (Vitali and others 2009). Several health products have now become available. Biscuits have been suggested as a good way to use composite flours as they are ready-to-eat, provide a good source of energy, and are consumed widely throughout the world (Arshad and others 2007). Examples of innovations in biscuit formulations include the use of non-cereal ingredients for gluten-free biscuit manufacture, partial replacement of fat and sugar with mimetic ingredients, and the incorporation of novel ingredients that are beneficial to health or are nutraceuticals.

Gluten-free biscuits

Celiac disease is an antibody-mediated enteropathy that presents permanent intolerance to ingested gluten from wheat, rye, barley, and other closely related cereal grains (Zandonadi and others 2009). The only effective and available treatment for celiac disease is strict adherence to a gluten-free diet throughout life. As awareness of gluten allergy/intolerance increases, and with better diagnostic tools to detect celiac disease, sales of gluten-free products are projected to grow at an annual rate of 25% for the next few years (Siddiq and others 2010; Zucco and others 2011).

In the manufacture of gluten-free biscuits, the wheat flour needs to be replaced by other ingredients. These ingredients need to replace not only the starch, which is normally delivered by the wheat flour, but also the protein fractions. In the early 2000s, gluten-free biscuits that could be included in the diet of patients with celiac disease were commercially available. However, they were often based on pure starches, resulting in a dry, sandy mouthfeel (Gallagher and others 2004). The key to success for gluten-free biscuits is that in contrast to bread, the gluten network in biscuits needs only to be slightly developed for the dough to be cohesive without being too elastic (Contamine and others 1995). This is an advantage when developing biscuits from gluten-free ingredients and allows successful work with many different ingredients and combinations of ingredients (Schober and others 2003). Most gluten-free breads have been made by replacing wheat flour with sorghum, pearl millet, brown rice flour, corn starch, potato starch, soya flour, and buckwheat flour or their combinations. Some of the replacements have been shown to be desirable, for example, replacement of wheat flour by amaranth flour, which has the added nutritional properties of amaranth containing methionine, cysteine, lysine, vitamins, and minerals (Hozova and others 1997). Sorghum flour is becoming increasingly common in gluten-free baked goods, mostly because it has similar nutritional properties to wheat, is a light color, and has a bland flavor (Lows 2003).

High protein biscuits

Pulse products could also be used as a source of protein to fortify biscuits. Tiwari and others (2011) prepared protein-enriched biscuits by substituting wheat flour with dehulled pigeon pea (*Cajanus cajan* L.) flour (PPDF) or pigeon pea by-product flour (PPBF).They found that the protein content of biscuits fortified with PPDF and PPBF increased by 1.3 and 1.4 times, respectively, compared to a control, along with a significant increase in fiber content. The fortification of biscuits using chickpea and broad bean flours as well as isolated soy protein isolates was also reported in an earlier investigation (Rababah and others 2006). It should be emphasized that the nutritional, physical, and sensory characteristics of such biscuits would depend on both the physicochemical properties of the legumes used in the formulation, and the processing method used to prepare the legume flour.
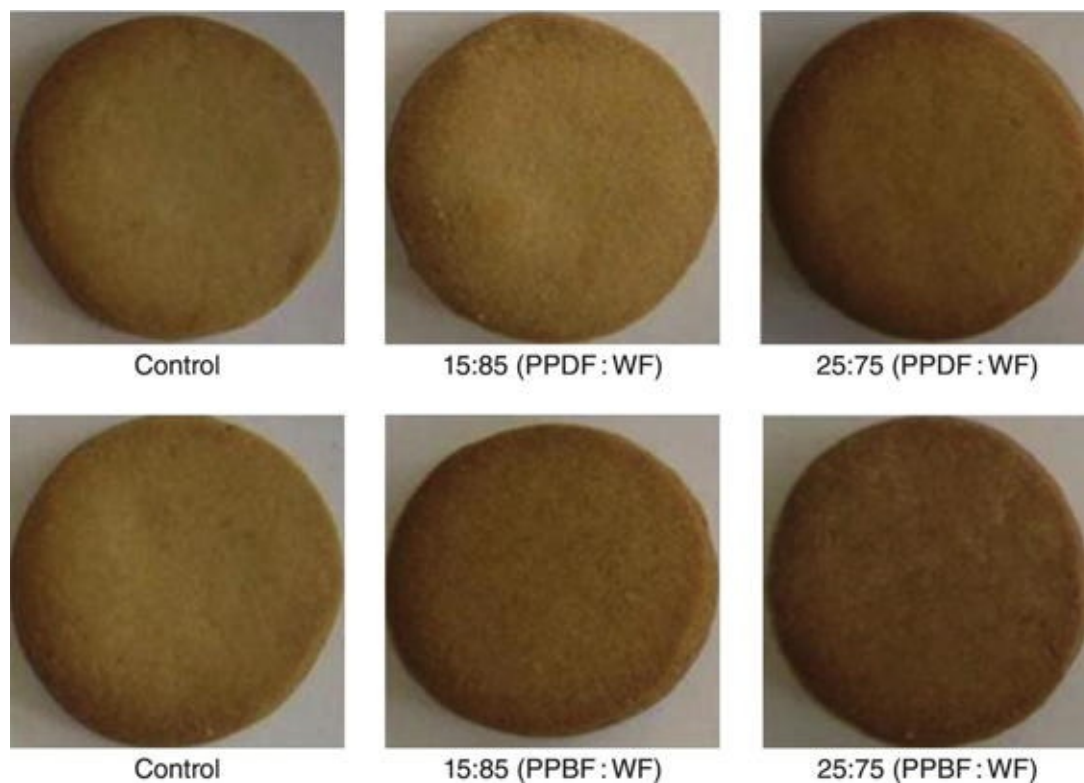
Figure 33.5 Biscuits made from 100 : 0 (control), composite flour of pigeon pea dehulled flour (PPDF) and wheat flour or pigeon pea by-product flour (PPBF) respectively. (Tiwari and others (2011). Reproduced with permission of Elsevier).

Pulse malts made from flour of refined wheat flour, an all-purpose wheat flour, with finger millet–pulse malt, wheat–pulse malt, 40% pulse malt, and 40% pulse malt with vanilla flavor have also been used to successfully increase the protein content of biscuits without adversely affecting the sensory attributes or the baking characteristics (Vaidehi and others 1985). The use of composite flours prepared from wheat, greengram, bengalgram, and blackgram flours have been studied by Singh and others (1993) for the preparation of biscuits. They observed that wheat flour containing bengalgram and blackgram flours adversely affected the top grain, texture, and color of biscuits, while those made with higher levels of bengalgram (more than 15%) were tough and difficult to break. In general, acceptable biscuits can be prepared from wheat flour supplemented with pulse flours at levels up to 15%.

Fiber-enriched biscuits

The term dietary fiber (DF) refers to a vast range of biophysically and biochemically divergent compounds, with varying effects on physiological parameters (Brownlee 2011). Dietary fiber

impacts all aspects of gut physiology and is a vital part of a healthy diet. Bakery products are generally deficient in DF due to the use of refined wheat flour as a basic raw material for their preparation. The addition of brans and gums to bakery products is one of the approaches normally adopted to increase their fiber content. The possibility of utilizing celery spent residue (CSR), a by-product from the spice industry, to enrich the nutritional characteristics of biscuits for dietary fiber, protein, and minerals, was recently studied by Sowbhagya and others (2011). They reported that acceptable quality biscuits could be produced with CSR up to 7.5% with increased protein, dietary fiber, and vital minerals such as calcium, iron, magnesium, and zinc. It has also been shown that high fiber biscuits can be prepared by replacing wheat flour with steamed bagasse at a 10% level (Sangeetha and others 2011). Biscuits prepared from steamed bagasse (10%) along with additives have been shown to be highly acceptable. Farinograph characteristics of wheat flour–bagasse blends show that the mixing profile weakens with addition of bagasse.

With an aim to develop nutritionally and functionally improved biscuits, Vitali and others (2009) supplemented standard wheat flour based recipe with inulin (10.5%) in combination with one of the following raw materials: soy flour, amaranth, carob (24.5%), apple fiber or oat fiber (16.5%).The total dietary fiber content in relation to reference biscuits was found to have increased by up to 30.9% (sample with amaranth) to 130.6% (sample enriched with oat fiber).

Antioxidant-enriched biscuits

The autoxidation of fats and oils in biscuits may be prevented by incorporating oxidation inhibitors or antioxidants. Besides this, antioxidative capacity is a very important aspect of the functionality of food as much scientific evidence indicates that food antioxidants play a paramount role in the prevention of different types of cancer and coronary heart diseases (Marnett 2000). Adding green tea extract (GTE) to biscuits not only improves their shelf-life (by preventing rancidity), but also adds a healthy appeal in the consumer's mind; such foods are popularly known as functional food (Sharma and Zhou, 2011).These effects are mainly due to the phenolic compounds present in green tea, which are well known for their antioxidant activity. Recently, Sharma and Zhou (2011) incorporated GTE into biscuit as a source of tea catechins. They observed that the stability decreased as baking progressed and increased as the concentration of GTE was increased in the biscuit dough. The stability of (−)epigallocatechingallate also increased as the pH of the dough was reduced and made less alkaline.

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34
Pastries

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Introduction

The origin of puff pastry and Danish pastry is thought to be the Turkish *baklava*. Baklava is a rich, sweet pastry made of layers of phyllo pastry filled with chopped nuts and sweetened with syrup or honey. It is characteristic of the cuisines of the former Ottoman Empire. Phyllo dough is a paper-thin sheet of unleavened flour dough used for making pastries. By adding yeast to the dough, puff pastry becomes Danish pastry.

In Scandinavia and in Denmark in particular, the term *Danish* pastry is not used. In these countries bakers talk about *wienerbrot* which literally means "bread from Vienna". In French the term used for Danish pastry is *viennoiserie*, again referring to Vienna as the origin of these products. In Austria itself it is called *Plunder*.

It is generally thought that the croissant originated in France. While traditionally ascribed to the French painter and cook Claude Gelée who lived in the 17th century (the story goes that Gelée was making a type of very buttery bread for his sick father and the process of rolling the butter into the bread dough created a croissant-like finished product), the origin of the croissant lies in Vienna. The shape of the croissant is a crescent moon and was first made by the bakers of Vienna during the 1683 siege of their beloved city by the Ottoman Empire. They made a *Plundergebäck* in the shape of a crescent moon to betray the position of the Ottoman army. Years later when the French queen Marie-Antoinette (1755–1793) visited Vienna, she fell in love with the product in the shape of a half moon or *lune croissant* in French, hence the name *croissant* in French.

It is important to understand that all these types of products (puff pastry, croissant, Danish pastry) are made by creating alternating layers of dough and fat by folding and rolling the dough.

Raw materials and recipes

As with most bakery products, there are as many recipes as there are bakers. Therefore the following recipe is just an illustration of a possible – but excellent – recipe for Danish pastry (Table 34.1) and for puff pastry (Table 34.2).

Table 34.1 Recipe for danish pastry

Ingredient	Quantity (kg)	% of flour	% of total
Flour	5.000	100	49.7
Water	1.500	30	14.9
Whole eggs	0.500	10	5.0
Milk	0.500	10	5.0
Yeast	0.250	5	2.0
Sugar	0.200	4	2.0
Salt	0.100	2	1.0
Subtotal	8.050	–	–
Roll-in fat	2.000	40	19.9
Total	10.050	–	100.0

Table 34.2 Recipe for puff pastry

Ingredient	Quantity (kg)	% of flour	% of total
Flour	5.000	100.00	43.5
Water	2.500	50.00	23.5
Salt	0.050	1.00	0.4
Subtotal	7.750	–	–
Roll-in fat	3.750	75.0	32.6
Total	11.500	–	100.0

Levels of ingredients may vary slightly due to the richness desired for the finished product. The amount of roll-in shortening used in relation to dough is important to the richness of the dough. Some of the standard amounts of roll-in shortening used per kilogram of dough are:

- lean Danish: 12.5–17% (i.e. 125–170 g/kg dough);
- medium Danish: 18–25%;
- rich Danish: 26–35%.

Flour

Quality, like beauty, is in the eye of the beholder. One doesn't look at the different strokes the artist has put on the canvas when looking at a painting, or listen to the separate notes when

one listens to a piece of music. No, one enjoys the ensemble of the work. One cannot discuss quality without defining quality for what purpose. This is particularly true for biological materials such as wheat flour. A quality flour that is good for producing white pan bread is not necessarily good for producing a sugar-snap cookie. Yet to the layman or casual observer, all wheat flours look alike.

There large differences found in the quality of wheat flour between bread, cake, pastry, and cookie flours, but differences are also found within each of those types. Taking pastry flour as an example, good-quality flour for producing puff pastry is certainly different from that intended to produce croissants or Danish pastry. It is also true that a good-quality pastry flour for line 1 in plant A is not necessarily a good quality flour for line 2 in the same plant. Differences in the equipment that make up the line, or even the physical layout of the line, will demand that the flour be different to perform at its optimum. The same would certainly hold for different plants. The variation can be true even if the plants contain the same equipment and have essentially the same layout. The rheological properties of dough are greatly affected by their temperatures. Thus, a plant in a tropical country may need different flour than a similar plant in Scandinavia or northern Canada. It is also true that the relative humidity of the location is important as it controls how much water is lost from the doughs during processing.

Bread flour with protein content of 11.5–12.5% is normally acceptable for the production of pastries. If the protein content is too high, the Danish will be tough to eat. Strong flour can be blended with 30% pastry flour to improve extensibility of dough during laminating.

During lamination, the flour must provide the gluten structure to form a strong dough film that is able to entrap the water vapour as it is formed during baking. Good bread flour with a protein content of 11.5–12.5 % and an ash content of not more than 0.5% will usually produce puff pastries of good volume and with a very flaky texture. Flours with a higher ash content often lack extensibility during sheeting and make-up. Higher protein levels tolerate slightly more lamination, but may not produce a better pastry.

Fat

A distinction has to be made between roll-in fat and the fat that is sometimes added to the dough as such.

The roll-in fat can be butter or margarine at a dosage level of as much as 50% of flour weight. Fat contributes significantly to the flavour and colour. Butter is preferred but cost and limitations with processing temperature range mean margarine is frequently used.

Butter is an excellent roll-in fat. It is functional and contributes a pleasant taste, aroma, and mouthfeel to the pasty. For good performance, however, butter must be processed within the relatively narrow temperature range of 15–20 °C. When butter warms to 21–22 °C or more, it becomes soft and is absorbed by the dough during lamination.

The fat added to the dough improves dough handling properties and the tenderness of the pastry crumb. The added fat can be butter in butter dough or margarine or vegetable shortening in regular pastry dough. Amounts can range from 8% (lean dough) to 20% (very rich dough). While the major amount of fat used in puff pastry is the fat "rolled" into the dough (discussed later), a lesser amount (0–20%, flour basis) is usually added directly to the

dough. Dough fat serves to lubricate the gluten structure and facilitates the laminating process. However, good-quality pastries can be produced without dough fat. When butter is used as a roll-in fat, then butter is usually also used as dough fat. However, doughs made with a salted margarine or butter may require a slightly longer mixing time than doughs made with regular shortening since salt retards gluten development.

In many bakery products, fat is layered between sheets of dough, and this is manipulated to make a dough sheet consisting of up to 100 alternating layers of dough and fat. Such roll-in doughs include Danish pastry, puff pastry, and croissants. The dough is mixed, divided into pieces of about 10 kg each, and then cooled to 5–10 °C in a retarder. The cooled dough is rolled out, 2–3 kg of fat is spread over part of the sheet, and the dough is folded over to cover the fat. The "sandwich" is then rolled out and folded; this is repeated several times, often with a retarding step included to keep the dough/fat mass cool.

The primary goal during the roll-in process is to preserve the structure of alternate layers of dough and fat. There are several important factors to consider in selecting the correct shortening or margarine for such a process. Some of them are: solid fat index (SFI) and plasticity of the fat; complete melting point of the fat; consistency (softness) of the dough; retarder temperature; number of folds given to the dough before returning it to the retarder; and proofing temperature. Many of these factors are unique to a given product in a particular bakery, and they influence the specification for the roll-in fat which gives the best final product in that bakery.

The dough for Danish pastry contains higher levels of sugar and water than a bread dough, making it quite soft at the usual mixing temperature of around 20 °C. After it is mixed (the gluten matrix is fully developed), it is divided and cooled as described earlier. The cooling and rest time (during which some fermentation occurs) makes the dough cohesive enough to handle, but if it is over-worked or allowed to warm up too much during the roll-in step, it again becomes soft, sticky, and easily torn. The plastic range of the roll-in fat must be rather broad. The consistency of the fat should nearly match that of the dough across the temperature range, which usually includes the temperature of the retarder (on the cool end) to room temperature or above. If the fat is significantly harder than the dough at the cool temperature, then when retarded dough is rolled out, the fat does not spread into a uniform layer between the dough layers, but is likely to tear holes in the dough sheet.

If the fat is softer than the dough at room temperature, then as the dough mass warms up (during rolling and folding), the shortening soaks into the dough, the adjacent dough layers knit together, and the layering effect is lost. The proper plasticity of roll-in fat requires a relatively shallow SFI profile and stabilization in the β crystal phase. The latter is particularly important. If the shortening has begun to transform to the more solid β phase, the additional hardness due to β crystals will cause excessive tearing during roll-in. The melting point of the fat must be higher than the proofing temperature for the Danish. If the proof box temperature is above the fat melting point, the fat layers turn to oil. This allows the dough layers to knit together to some extent during proofing, and the final product is less flaky than desired. As a general rule, the complete melting point should be at least 5 °C higher than proof box temperatures.

A standard all-purpose shortening having a complete melting point of about 45 °C usually works well in most Danish pastry production lines. This gives a flaky finished product. Some manufacturers use an emulsified shortening containing 3% monoglycerides, but with similar

SFI and melting point specifications. This produces a Danish having a somewhat gummier mouthfeel, which is preferred in some parts of the country.

Croissant dough is similar to Danish dough, although it generally contains less sugar and water, so it is firmer at the optimum mixed dough temperature of 20 °C. As with Danish, the dough pieces are usually retarded before roll-in is begun. The best quality croissants are produced using unsalted butter for roll-in. The amount used varies from 20 to 35% of dough weight; higher levels give a product that has less volume and flakiness, and is often perceived as greasy in the mouth. The optimum is usually about 25% roll-in fat.

The factors involved in successful processing of croissants are similar to those discussed earlier for Danish pastry. Because butter has a steeper SFI curve than all-purpose shortening (it is much harder at retarder temperatures), more care is required to prevent tearing the dough as it is being rolled. The melting point is lower than that of shortening, so proofing temperatures are lower than for Danish. Puff pastry margarine is an acceptable substitute, although it does not contribute as much flavour as butter. Since puff pastry margarine has a higher melting point, the proofing may be done at a higher temperature (and for shorter times) if time is a factor.

Rolled-in doughs that contain no yeast (puff pastry) depend upon steam generation in the oven for their leavening. Usually margarine (which contains about 17–20% water) is used for the roll-in fat for these doughs. The water is trapped and held in the fat layers in the dough. It evaporates and expands in the oven, giving an expanded structure to the final product. If the fat portion of the margarine is too soft, the water migrates into the dough during the roll-in step, and the leavening action in the oven is decreased. Puff pastry margarine has a higher SFI curve than all-purpose shortening, and it is slightly more brittle during roll-in. In this case a smooth, continuous layer of fat between dough layers is not particularly desirable. The roll-in process is adjusted to achieve numerous discrete particles of margarine between the dough layers. These produce larger voids in the finished product, which is desirable in a puff pastry.

Whole eggs

Liquid whole eggs not only add liquids to the dough and strength to the baked product, but also contribute to crust colour. Dried whole eggs function as well. Puff pastries prepared with 10% (flour basis) liquid whole eggs develop a better crust colour and require a slightly lower baking temperature than the same products containing no eggs. The egg protein participates in the browning (Maillard) reaction that produces the attractive golden-brown crust color. The crust color also helps to mask the greying effect caused by fat crystallization (fat bloom) as the pasty ages.

If higher levels of sugar and shortening are used, the eggs should also be used at higher levels to carry their weight. Eggs are primarily used for structural strength in Danish and may be fortified with whites for added strength or yolks for added tenderness.

Sugar

In this application, sugar comprises granulated sugar (sucrose) and high-fructose corn syrup (HFCS). Dextrose (glucose) may be used at levels not exceeding 10% of the flour weight.

Higher levels of dextrose crystallize as monohydrates, causing the product to become dry and crumbly. However, sucrose and HFCS may be used interchangeably as long as adjustments are made for the 29% moisture content in HFCS.

Sugar affects the dough water absorption. Rich doughs (high sugar content) tend to absorb less water than lean doughs, but they also slow down yeast activity. To off-set this effect, the yeast is normally increased as more sugar is added to the dough. Generally, the amount of compressed yeast added to sweet doughs is about one-third the amount of sugar solids in the formula.

Processing

The puffing action in puff pastries involves neither a chemical leavening agent, nor microbiological fermentation as occurs in yeast-raised bread doughs. The puffing depends solely on the significant increase in volume when moisture, turning into steam, becomes trapped between dough layers separated by thin films of fat resulting from the laminating process.

The ability of the "roll-in-fat" to keep dough layers separated, primarily determines the quality of puff pastry. During the laminating process, dough layers are reduced to an average thickness of about 0.015 mm. At this thickness, the gluten structure in the dough assumes a two-dimensional orientation, as compared to the three-dimensional cell structure in most other doughs and batters.

The two-dimensional orientation of the gluten structure resembles that of a film and is able to entrap steam during the baking process. This process finally produces the flaky structure in the pastry during the baking process.

Danish pastry on the other hand is a combination of puffing action and fermentation.

The processing is composed of the following steps:

- dough mixing
- dividing of the dough in pieces or dough sheets in the case of automated equipment
- laminating
- make-up
- filling and/or decoration: can happen before or after proofing
- proofing in the case of danish pastry or croissant
- topping
- baking
- cooling
- icing.

Some of these steps are discussed in detail.

Dough mixing

The dough ingredients are all combined and mixed in one stage. As there is still further gluten development during the lamination stage, the mixing of the dough should not be overdone. Doughs are usually mixed until the gluten structure is partially developed; full gluten development occurs when the dough is sheeted for laminating.

Depending on the type of make-up used, production facilities may be confronted with a large amount of scrap dough. The scrap goes into special baked snack items, or they may get incorporated in fresh doughs. Large operations with automated laminating equipment prefer to add their scrap to new doughs near the end of the mixing cycle. Since scraps already

contain the full amount of roll-in fat, there is usually no additional puff paste added for this dough portion. Care must also be taken that the scrap dough contains no traces of fillings because remnants of a pasty filling may cause dark spots to form on new pasty during baking. The basic recipes given earlier should be adjusted for fat and sugar according to the amount of scrap used in a fresh dough.

Alternatively, the scrap dough can be made into some kind of sourdough by adding water and leaving the mixture for 24 h in controlled temperature conditions. This procedure improves the taste and the shelf-life of Danish pastry.

Lamination

There are basically three methods to make puff pastry and Danish pastry: French method, Dutch method, and the extruder system.

For the French method, the roll-in fat is spread or spotted over two-thirds of the dough which has previously been weighed and sheeted into a rectangular shape. The uncovered portion of the dough sheet is folded over half of the fat covered portion and the other half is then folded over the doubled up dough portion. This results in three layers of dough with two layers of fat sandwiched between them. After 20–30 min rest in the retarder, the layered dough is sheeted to an uniformed thickness of 1.5–2.0 cm. The reduction of the thickness should happen slowly and smoothly by using a roller table and should not be too abrupt.

The dough rest allows the dough to relax and gives the yeast the opportunity to adapt to its new environment.

The dough piece is then given a three-fold by folding one-third of the dough over the centre section and then the third section of the dough is folded over the doubled up section. The dough should rest again in a retarder for about 20–30 min. This process is repeated a number of times to create more layers. The number of folds varies based on the amount of roll-in fat and can be as much as 264 layers for puff pastry (Table 34.3). For Danish pastry 48–64 layers are normally sufficient.

Table 34.3 Folds and fat layers in laminated dough

Number of folds	Number of layers
2 × 3 × 3	18
2 × 3 × 4	24
2 × 3 × 3 × 2	36
2 × 3 × 3 × 3	54
2 × 3 × 3 × 4	72
2 × 3 × 4 × 4	96
2 × 3 × 3 × 3 × 2	108
2 × 3 × 3 × 3 × 3	162
2 × 3 × 3 × 3 × 4	216

In a second method, the "Dutch system" (also sometimes called the Scottish method), a higher melt point roll-in shortening is combined in the mixer with a semi mixed dough. This

method utilizes the same technology as used for mixing pie doughs. The roll-in fat must be firm and is cut into small cubes measuring about 3 cm on each side. These chunks are dispersed in the flour before the liquids are added. After all the ingredients are combined, water and eggs included, they are blended together without significant gluten development. The dough is then allowed to hydrate properly for about 30 min before lamination. Then, the dough is sheeted out to the desired sizes, folded, and retarded. From here a manual or semi-automated system is used for the remaining process.

A third method, the "extruder system," has arisen with the use of high speed sheeters. In this system, the roll-in shortening is applied to the dough piece by a shortening extruder. The dough is cut, folded into a three-fold or four-fold unit, quarter turned, and sheeted again. The dough is retarded for up to 6 h, and then it is returned to the make-up line where it is sheeted and folded again. From here the dough is retarded for an additional period of time before the make-up process.

Equipment is available to laminate pastry dough on a continuous basis. There are essentially two different systems used for incorporating the roll-in fat and two systems for laminating. The products manufactured with this type of equipment are generally intended for wholesale distribution, and their flakiness and size are limited to reduce breakage during shipment.

Since puff pastry doughs become less extensible with increased lamination, most automated laminating lines utilize two reduction (sheeting) and laminating stations positioned in a 90° angle to each other to equalize directional stress in the dough.

The roll-in fat is either co-extruded on the inside of a hollow tube of extruded dough or deposited as a continuous layer of fat on top of a continuous layer of dough which is then covered with a second layer of dough. After some sheeting and cross-sheeting the laminated dough is folded in a back-and-forth motion on the slowly moving stacking table. The speed of the stacking table conveyor determines how much each layer overlaps the previous layer and the degree of lamination. The dough can be stacked as high as 15 cm without causing problems at the reduction station, where a multiple roller system reduces the stacked dough to the desired thickness of about 1.5 cm. Since these rotating rollers move with the dough and the gap between them and the take-away conveyer section is gradually narrowing from roller to roller, this reduction in dough thickness is fairly stress-free and allows products with a regular shape to be obtained.

Make-up

After retarding the dough for several hours (or even overnight), the dough is ready for make-up. This happens best at a low temperature (± 15 °C). It is again important to reduce the thickness of the dough gradually using a sheeter to avoid rupture of the layers. The flakiness can be adversely affected if the dough is reduced too quickly. Once sheeted to the final thickness (2–3 mm) there are a number of ways in which the dough can be made up, including crimping, curling, filling, folding, and twisting depending on the desired end product.

Fillings

Important is to remember that the water activity of the filling has to be studied as a function

of the type of product, the expected shelf-life, stability during baking, packaging, and so on. Water migration from the filling to the dough has to be considered.

The filling should contain sufficient sugar to avoid boiling (out) during baking.

Proofing

Proofing is a crucial step in the process. If the dough gets proofed when the temperature is too high, the roll-in fat may melt and bleed out of the product, resulting in a poor puff. Over-proofing can cause collapse of the product in the oven. Danish should be proofed at 26–29 °C with a relative humidity of 65–70% for 60–75 min. They should be proofed until 2–2.5 times their original size.

Baking

As for all bakery products, baking time and temperatures are dependent on the type of oven, the size and shape of the product, and the type and quantity of the filling.

Danish pastries are usually baked at slightly lower temperatures than equivalent products made from regular sweet doughs. Also, leaner doughs are baked slightly hotter than rich, high-sugar doughs. The baking temperature also varies with different oven types. For the same temperature settings, rack and other convection ovens tend to bake hotter than regular gas ovens (reel and traveling tray). Electric deck ovens often bake cooler and require longer baking times.

Danish sweet rolls may be baked at 200–210 °C in a gas-fired reel oven. Coffee cakes should be baked a little cooler, at 185–200 °C. Some toppings tend to char easily and require lower temperatures. The baking times vary not only with the baking temperature, but also with the size of the baked food. A 50 g Danish pastry is usually baked for 15–17 min at 200 °C.

Troubleshooting

An overview of a series of possible problems that may arise during processing of pastries, with their remedies, is given in Table 34.4.

Table 34.4 Troubleshooting

Problem	Probable cause	Remedy
Butter breaks through the dough	Butter too cold Dough too soft Abrupt sheeting	Condition the butter before use to 14–16 ºC Reduce the water content of the dough to obtain the same consistency of the butter use gradual and even sheeting reduction
Butter oozes out from dough	Butter too warm Dough too warm Dough too tight	Condition the butter before use to 14–16 ºC Chill the dough Increase water content
Butter melts during proof	Proofer too warm Insufficiently laminated	Reduce proofer temperature Laminate and fold more to obtain more layers
Baked pastries have odd shape	Irregular lamination Butter too hard Oven too hot Dough rolled out too thinly	Condition the butter before use to 14–16 ºC Bake at 200–210 ºC Use gradual and even sheeting reduction
Bakes pastries show fatty patches inside	Insufficient lamination Excess roll-butter	Laminate and fold more to obtain more layers Reduce roll-in butter
Pastry sticks to the sheeting rollers	Insufficient dusting Bakery too warm	Use more dusting flour during sheeting Work in an air-conditioned room at 18–20 ºC
Tough end product	Too little fat (roll-in and/or dough fat) Baking temperature too low	Increase the butter content Bake at 200–210 ºC

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35

Pretzel Production and Quality Control

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Introduction

Hard pretzels were introduced to the United States in the 1860 s at Lititz, Pennsylvania, and have since become a very popular snack food. Pretzels are said to have had their origin when a 12th century monk rewarded children who recited their prayers properly. The crossed center of the pretzel form, legend has it, represented the folded hands of prayer. Pretzels are acknowledged as a healthful snack and are gaining popularity around the world. Pennsylvania ranks first in the nation in the production of snacks, especially pretzels. Over 23 pretzel manufacturing companies are located in Pennsylvania, and they sell pretzels in more than 11 countries.

Since the 1980s, significant advances have been made in automating pretzel production. Considerable improvements have been made to the equipment used in plants, including high-speed mixers, pretzel dough cutter systems, automated pretzel forming machines, and pretzel ovens. Several patents have also been granted for new methods in hard pretzel manufacturing.

Despite the popularity of pretzels as a snack and technical advancements in their production, very little research has been conducted on this product compared with the research done on other products including cookies, crackers, and other snack products. Hard pretzel production was, and still is, based more on the experience of the operator than on science, despite the automation of the production process. Manufacturers still produce pretzels using a traditional formula (Table 35.1). Pretzels typically come in a variety of shapes and sizes including rods, sticks, and other specialty and seasonal shapes.

Table 35.1 Hard pretzel formulation.

Ingredients	Quantity (kg)
Flour	100.0
Water	42.5
Sugar	2.5
Oil	2.5
Yeast	0.28

Structure and formulation

Structural description of pretzels

A good quality pretzel could be defined as one where there is a balance between gluten and starch functionality in the product. It has been shown that not all starch granules are completely gelatinized (Fig. 35.1) in a good quality pretzel (Seetharaman and others 2004). The structural integrity of pretzels is compromised if the gluten functionality or the starch functionality dominates. For example, when lower levels of water are added to the dough, gluten development is limited and the starch appears to anneal and form a glassy matrix, resulting in pretzels that are brittle. In contrast, with higher levels of added water, gluten development is adequate, but the extent of starch gelatinization is also higher, resulting in a harder, unacceptable pretzel with a retrograded starch matrix (Fig. 35.2).
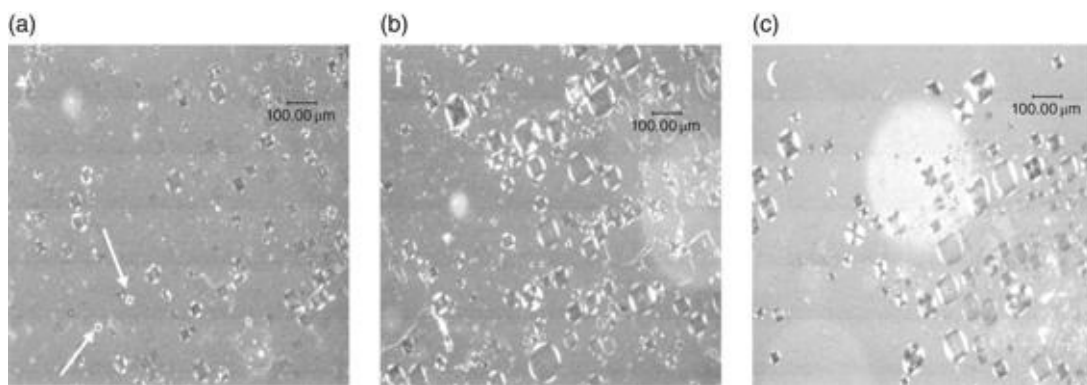
Figure 35.1 Polarized light microscopy (10X) of low water (left panel), control (center panel), and high water pretzels (right panel). Ungelatinized starch granules are indicated by arrows.

(a)

(b)
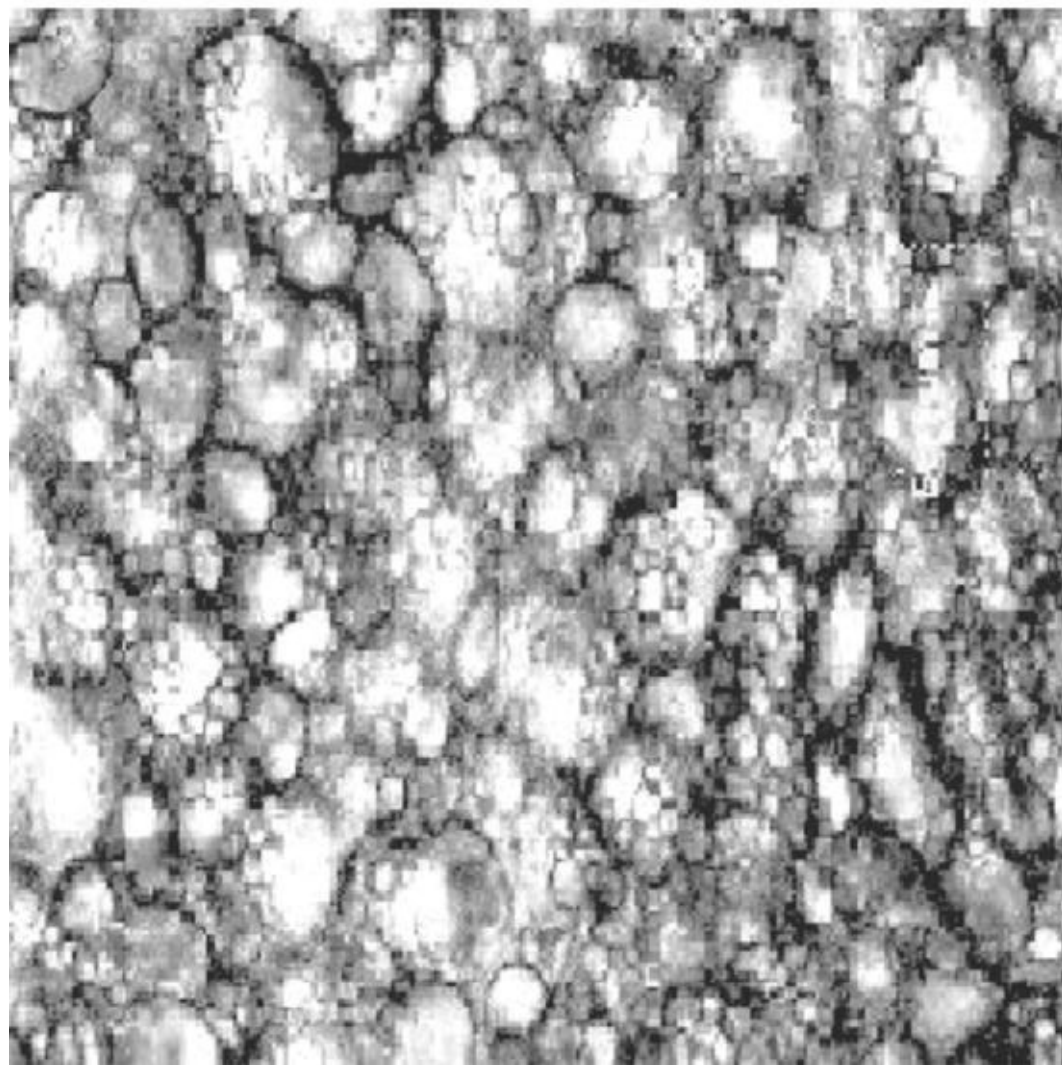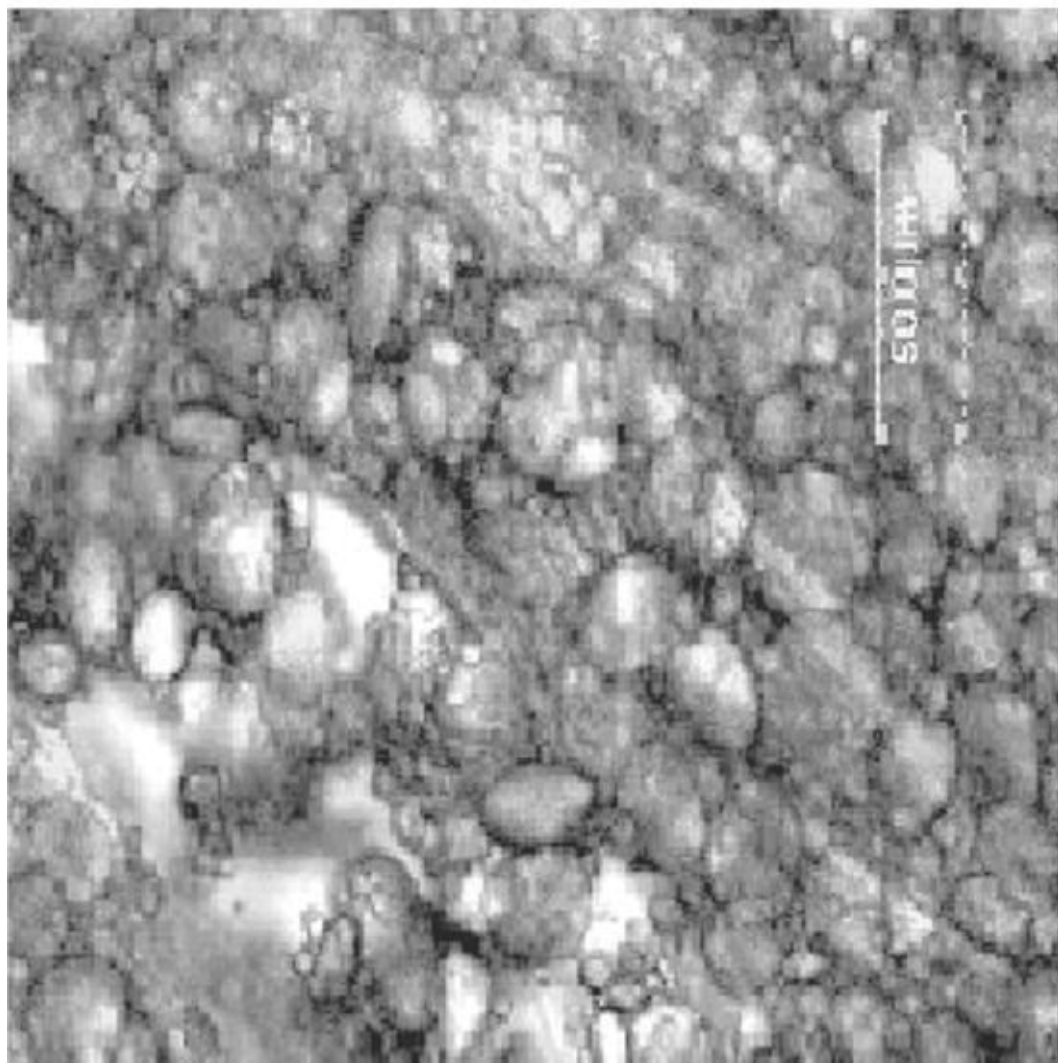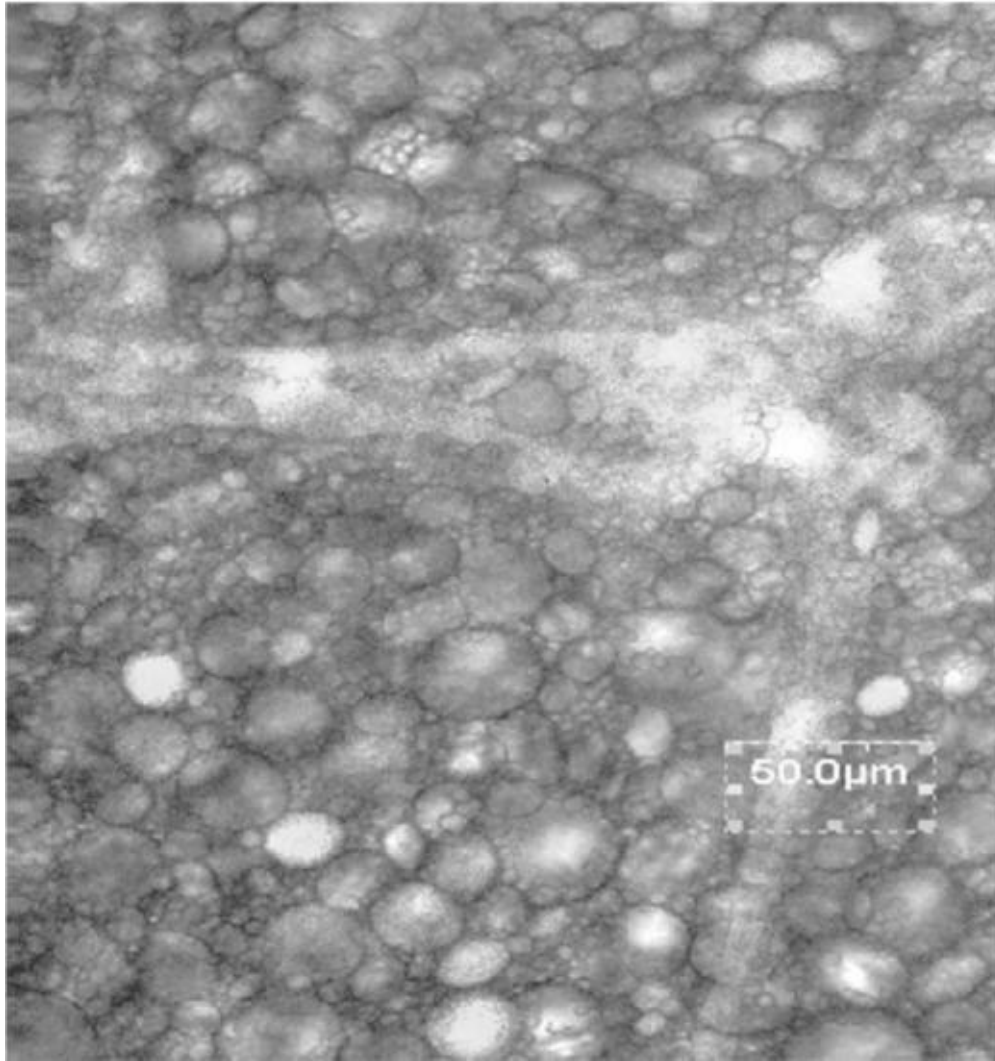
Figure 35.2 Gluten development in pretzels.

Formulation

Pretzel production is simple and basic. Flour is the major, and the most important, ingredient governing the functional properties of pretzels. Pretzel formulations can include either a chemical or yeast as the leavening agent. The particular choice of the leavening agent is dependent on each company and on the shape of the product. The addition of active yeast could contribute to the flavor, but care must be taken to control the proofing time. For specific products such as sourdough pretzels, a starter culture is added similar to that used in bread making, and the dough is proofed overnight.

Flour quality

Flour is the major and most important ingredient governing the functional properties of pretzels. The flour used by the modern automated pretzel industry is still the same as that used when pretzels were made by the old-fashioned, hand-rolling method. Typically, the flour of choice for pretzel production is soft red winter wheat with a protein content of about 9%. The influence of flour quality on pretzel quality is as a function of its protein content, its protein quality, and the levels of damaged starch and pentosan. Protein quality is a function

of glutenin and gliadin functionality. In industry, typically specified amounts of water and energy are applied to make dough. These parameters are specific to each company, based on the flour they use and the particular product characteristics they aim to produce. The operators then use their judgment to add more water or adjust the mixing time. In a recent study conducted in his laboratory, the author (and colleagues) determined that there was a high degree of variability observed in flour properties received at each company (Seetharaman and others 2002). The solvent absorption data related to glutenin quality showed the most variability, suggesting significant impact on the functionality of flour protein. Furthermore, control of the moisture content of flours appears to be more important than control of protein content, as long as soft red wheat flours are used. Critical evaluations of farinograph specification sheets from the flour mill should also be conducted to estimate the amount of added water and the optimal mixing time required to achieve good quality dough.

Research has shown that pretzel hardness exhibits a positive correlation with flour protein content, dough water absorption level, dough development time, dough stability, and the solvent retention capacity of flours in different solvents. These observations can be adapted and used as a quality assurance test within a production facility.

Pretzel processing

The pretzel production process includes dough mixing, forming/shaping using an extruder at low pressure, cooking in a hot alkali solution, and baking. The baking process is divided into two steps: (1) first rapid baking at a high temperature and (2) a slower, lower temperature for drying to reduce moisture content to < 4%. The processing steps are described below to facilitate a better understanding of this ancient snack food under a modernized manufacturing environment. The process flow chart is shown in Figure 35.3.
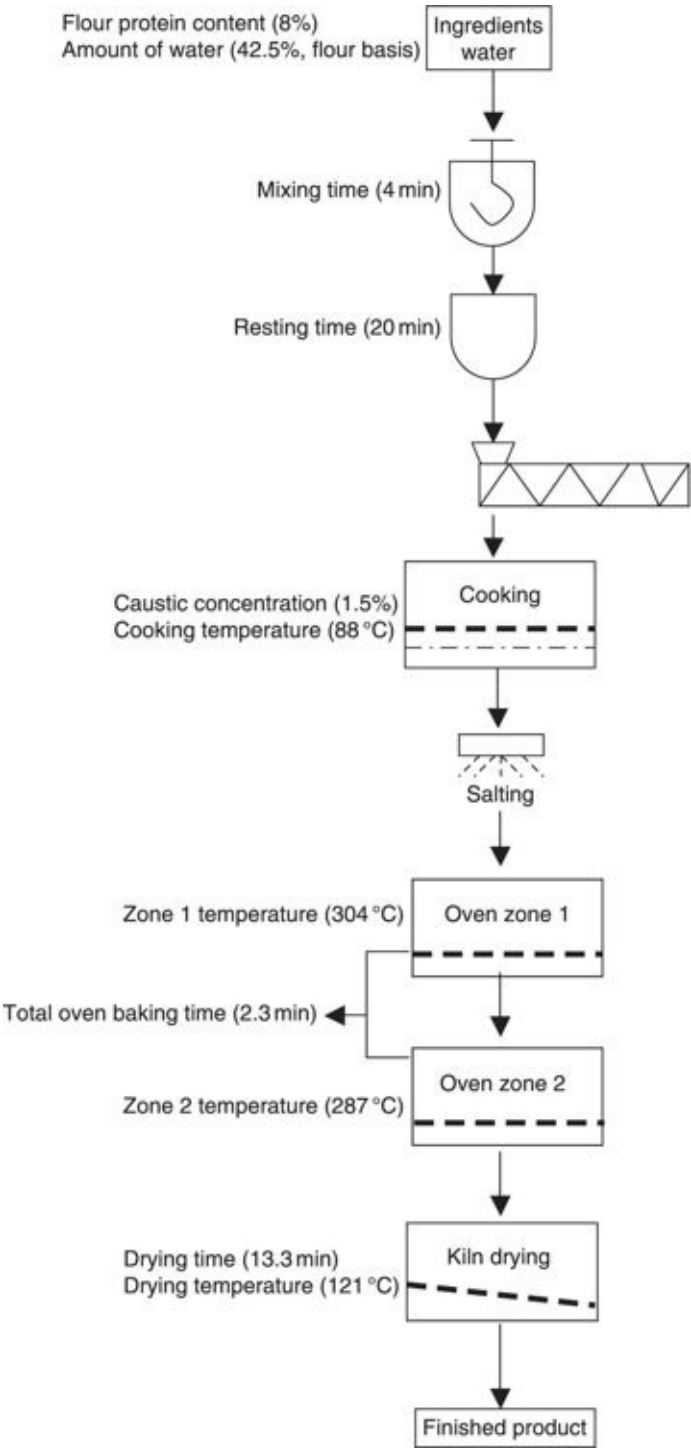
Figure 35.3 Process flowchart for pretzel production.

Dough mixing and resting

Dough mixing is a critical step in pretzel production. Pretzel doughs are typically drier, based on the water required by the flour for optimal gluten development. The pretzel industry uses many different types of mixers including batch mixers, high-speed mixers, and continuous mixers. The mixing time varies among companies based on the type of mixer, the flour properties, and operator judgment of the dough properties. Since pretzels are made using lower protein flours, they do not require longer mixing times. Furthermore, mixing time is critical since low protein flours have a lower mixing tolerance; that is, breakdown of gluten due to increased mixing time. The amount of water added and the mixing time are critical for optimal gluten functionality and dough functionality.

Dough temperature can be critical during dough shaping to facilitate uniform pressure at the extruder head and to retain the shape and integrity of the shaped dough. Typically a dough temperature around 32 °C is preferred, and this can be achieved by adding water at 38 °C during dough mixing.

Of equal importance is the resting time due to yeast activity and its effect on dough properties. Resting time includes the time from when the dough comes out of the mixer until it enters the cooker. Higher yeast activity promotes more gas production, which tends to disrupt the gluten structure. The ambient conditions in the mixing room also influence yeast activity. Warm and humid conditions in the room will promote greater yeast activity, thus requiring shorter resting time.

Dough forming and shaping

Extrusion is one of the most common technologies used to shape pretzels, although some larger sized hard pretzels are still mechanically rolled and shaped. During the extrusion process, the dough is passed under low pressure through a die consisting of several holes based on the size and shape of the pretzel. The strands or noodles of dough are then knit together in the die before being cut by the knife and dropped on the conveyor belt. It is recognized that extrusion contributes to further mixing of dough. The gluten strands are sheared and reformed during the extrusion process. Higher extrusion pressures have been suggested as a possible cause of pretzel crystallization, that is, breakage, but it is more likely that extrusion pressure is a symptom of dough handling conditions prior to reaching the extruder, including lower levels of water added to flour prior to mixing or lower dough temperature. Extrusion can also cause quality concerns in pretzels if the dough is overmixed prior to reaching the extruder, thus resulting in further breakdown of gluten due to shearing in the extruder. Special attention should be focused on maintaining the extruder heads and the cutting knife.

Cooking

The use of sodium hydroxide as a processing aid is unique to pretzels when viewed in the context of all baked goods, and thus pretzels can be differentiated from crackers or breadsticks. Cooking in a hot alkali solution prior to baking gives pretzels their unique texture and appearance (Groff 2001). The shaped pretzel dough typically passes through a solution of 1–1.5% sodium hydroxide at 93 °C and remains immersed for about 10–15 seconds. The pretzels are either dipped or sprayed with lye solution. Cooking in alkali solution gelatinizes the surface starch that forms the hard exterior crust of the pretzel when

it enters the oven. The gelatinized starch also undergoes Maillard reaction in the oven, giving pretzels a shiny brown color on the exterior surface with an alkaline pH and its opaque interior with an acidic pH. The gluten network is also broken under alkaline conditions due to protein hydrolysis. The typical brown color of pretzels is due to the reaction of carbohydrate and protein hydrolysis products and also potentially the reaction between these hydrolyzed products. Any changes in the temperature or strength of the cooking solution will alter the degree of starch gelatinization and, consequently, pretzel color and texture. It is necessary to maintain adequate depth of solution in the cooker so as to completely immerse the formed dough into the solution. Furthermore, the dipping temperature has to be above 70 °C to allow for starch gelatinization, without which the shaped dough will stick to the conveyor belt.

Salting

Following cooking, salt is typically sprinkled on to the wet dough surface. The particle size of the salt is important for visual appeal. This unit operation is also used to sprinkle sesame, mustard, or other toppings on the pretzel surface. The roller settings that deliver these ingredients should be adjusted based on the particle size of the topping used.

Baking and drying

The pretzel baking process is divided between an oven and a kiln. The oven/kiln is typically constructed in modular sections that are coupled together to meet specific production efficiencies. The temperature in the baking chamber and the kiln are set based on the particular type of product, size and shape of the product, and the volume produced. The pretzel moves through the baking chamber for 2–8 minutes, wherein product moisture is rapidly reduced to 8–10%. The product then enters the kiln, where it is further dried down to a final moisture content of < 4% over 6–45 minutes.

The oven serves several important functions including setting product structure, developing product color, and removing moisture from the shaped dough. The temperature zones within the oven and the proportion of radiant versus convection heat in each zone should be carefully controlled. The heat delivered in the first zone governs the extent of moisture removed and is critical in the setting of the surface crust. The heat in the subsequent zones should be lower in order to further remove moisture without forming blisters in the product. The extent of starch gelatinization is minimal in a good quality pretzel because of the rapid decrease in moisture content before the starch in the interior of the product can gelatinize. The product has a relatively hard surface as it enters the kiln, and therefore the kiln temperature is significantly lower than that in the oven to prevent burning of the product or creating cracks in the product. The final product moisture is critical since moisture content that is too low will make the product brittle, while moisture content that is too high will result in stale products over time.

Finished product conveying and packaging

Baked dry product is discharged onto conveyors leading to packaging machines. All transfer points must be gentle and smooth. Pretzels exiting the kiln quickly cool to less than 93 °C and are less susceptible to breakage since this is warmer than room temperature. However, as a pretzel cools to room temperature, it becomes more fragile and must be handled with greater

care (Groff 2001). Finished products are normally transferred from the dryer exit to a packaging machine by an inclined belt conveyor by using an oscillating motion conveying system.

Quality assurance critical control points

In each step of the process, parameters are set up based on experience and the wide variety of bake times and temperatures that are used in pretzel baking (Groff 2001). There are specific steps along the production route that it is critical to monitor in order to minimize production losses and maintain consistent quality.

1. Flour quality should be monitored, especially when changing suppliers.

2. Use the water absorption data and the dough development data from the Farinogram provided by the mill to determine the level of water to be added to the dough and determine the mixing time.

3. Monitor the dough extrusion pressure. This information will be indicative of any changes in dough rheology. This can be used as a guide to check if the dough properties are consistent.

4. Monitor alkali concentration and temperature. This is critical to achieve consistent product color, texture, and flavor.

5. Baking and drying temperatures should be monitored. The thermostat in the oven should be calibrated periodically so that accurate temperature is recorded.

A wide variety of baking times and temperatures are used in pretzel baking. Temperature control is critical for final product quality. Since different pretzels have typical heat transfer profiles peculiar to their shape and formula, temperature adjustment is essential to meet the heat requirement during processing. The heating parameters can also be adjusted to deliver products with different textures and flavor profiles.

Records should be maintained for quality control purposes. The final product moisture, usually controlled at 2–4%, is important for product quality and shelf life. Pretzels with too low a moisture tend to be very fragile during packing and transportation, while pretzels high in moisture content become stale during storage and thus will not be accepted by consumers. Pretzel color should also be monitored. Changes in pretzel color typically are a function of baking or drying time-temperature or are due to changes in alkali concentration. In a fully automated operation line, color monitoring and computer control of the complete process are possible.

Pretzel breakage

Besides general inconsistencies in quality or production efficiencies, pretzel crystallization is recognized as a particularly important problem typical for hard pretzel production. Crystallized pretzels are dense in texture and glassy in appearance. Pretzel crystallization can be predicted from the rheology conditions of dough following extrusion. Shaped dough exhibits visible color change, has a complete lack of elasticity and cohesiveness, and falls apart; and crystallization results in broken pretzels after baking (Groff 2001). Crystallized pretzel dough does not rise in the oven and develops a dense and translucent texture. Pretzels

become extremely brittle and break into tiny pieces after cooling, with breakage rates exceeding 50%. Crystallization can be eliminated by following a stringent quality assurance program that includes monitoring of incoming flour quality and adjusting the level of water added to dough and the mixing time. Research has also shown that the baking parameters can be adjusted to accommodate for variations in flour quality or other dough processing parameters (Yao and others 2005).

New product development

The pretzel industry has been slower to capitalize on consumer trends or produce innovative new products to increase profit margins. Pretzels, however, are ideal candidates for innovation. Novelties in the pretzel industry currently include new, and sometimes seasonal, shapes; new flavors and toppings; and pretzels with fillings including cheese or peanut butter. Opportunities exist to enhance the nutritional value of pretzels though the addition of nutritional supplements. Further opportunities exist to create pretzels with unique textural experiences. Pretzels also have the potential be a low (controlled) glycemic index product with some modifications. Further testing needs to be conducted in this area. However, any approach to innovation should incorporate the knowledge from the above sections and understanding of the specific changes that will result from the innovation.

Soft pretzels

Introduction

Soft pretzels are breadlike products with production methods similar to those of bread. The main difference is that shaped soft pretzel dough is typically dipped in a sodium bicarbonate solution. This gives the outer layer of the soft pretzels a shiny brown color with a slightly firmer texture. The soft pretzel market is dominated by retail outlets that bake and sell the products in stands. Soft pretzels are also produced in bulk, wherein the product is parbaked and frozen. The frozen product is warmed up at the retail outlet.

Production

Like breads, soft pretzels require flour of a slightly higher protein content than that used for hard pretzels. Typically, an 11–14% protein hard spring wheat flour is used for soft pretzel production. A typical soft pretzel formulation is listed in Table 35.2. Several optional ingredients can be used in the production of soft pretzels. Yeast is the common leavening agent, although baking powder is also used in some soft pretzels. Cysteine or sodium bisulfite is often added to break down the gluten and soften the dough, especially when the pretzel is shaped by hand. Dough conditioners can also be used to improve dough functionality and improve the texture of the product. Other ingredients including molasses or other sweeteners are also added to improve the color and flavor of the product. Following shaping, the dough is typically proofed for several hours to allow the yeast to raise the dough. The dough is then retarded under refrigeration conditions until baked. Prior to baking, the shaped dough is dipped in a sodium bicarbonate dip (1% concentration) at 90 °C for about 10 seconds. Salt is then sprinkled onto the dough surface. Baking is typically conducted in revolving ovens or in continuous single-pass ovens at about 260 °C for 5–7 minutes. The product should be cooled to room temperature prior to packaging. Large bakeries that produce parbaked frozen soft pretzels have an automated production line similar to that for hard pretzels. Following baking, the product is frozen rapidly to below –20 °C. The frozen product is packed and shipped frozen to the point of sale, where it can be reheated prior to consumption.

Table 35.2 Soft pretzel formulation.

Ingredients	Quantity (kg)
Flour	100.0
Water	45.0
Malt	2.0
Shortening	0.75
Yeast	1.5

Soft pretzels typically have a shelf life of less than 3 days and therefore are typically baked and sold at the point of sale. Limitations in product acceptability typically arise when the salted soft pretzels are stored in sealed bags. The salt melts due to the humidity in the bag and wrinkles the pretzel surface, decreasing its consumer acceptability.

A variety of new variations and products have been developed in recent years. Soft pretzel rods, hot dog buns, sandwich buns, and some filled pretzels have captured the market. All of these products are variations on the soft pretzel theme and are dipped or sprayed in an alkaline solution to give them the characteristic pretzel appearance.

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Bakery Products of Unconventional Flours

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Introduction

The food industry is constant changing and developing new products according to consumer needs. The baking industry is one of the most active, because bread is widely consumed in most homes throughout the world. However, for people who are overweight, obese or who have diabetes, consumption of traditional or normal bread is either prohibited or limited because its high content of digestible carbohydrates increases the glucose level in the blood. One alternative is to produce bread with high dietary fiber or high levels of indigestible carbohydrates, which can be considered as "healthy breads", and are also classified as nutraceutical foods. Nutraceutical foods are defined as "foods similar in appearance to conventional foods that are consumed as a part of the normal diet and have demonstrated physiological benefits and/or reduce the risk of chronic disease beyond basic nutritional functions" (Health Canada 1998). Nowadays, there are diverse bakery products that are elaborated using whole grain (oats, wheat, barley, rye) and a mixture of these (multigrain blends, oat fiber). Different investigations are focused on the effect of "healthy" ingredients on the sensory characteristics of bread, such as texture and loaf volume, and also on evaluating the acceptance of new ingredients by consumers (Athayde and others 2009; Calderon and others 2010; Okpala and Chinyelu 2011). In the same sense, diverse studies are being carryied out to develop new bakery products using unconventional ingredients with low amounts of digestible carbohydrates or with high amounts of slowly digestible carbohydrates. In relation to the digestibility of carbohydrates, there are many groups of researchers focused on slow starch hydrolysis and the low glycemic index characteristics of starch (Busken 2011). One factor that contributes to the decreased absorption of glucose into the blood is the regular consumption of dietary fiber and other food components such as resistant starch.

Most of the unconventional ingredients are raw materials and could come from agriculture-based industries, for example by-products of juice, such as orange bagasse or starch isolation, like some fibers. The use of by-products has two advantages: first, it uses a residue that contaminates the environment, and second, the cost is low. Other raw materials are those derived from unripe fruits that contain high amounts of starch, such as flours, which are prepared using either the pulp or the pulp and peel. Unripe fruits such as banana contain a high amount of RS (Bello-Perez and others 2010).

Legumes are characterized by having a high amount of dietary fiber and RS, which slow digestion, which may explain why people from countries in which legume consumption is high have a lower incidence of chronic degenerative diseases.

Fruits and legumes contain bioactive compounds that provide nutraceutical properties in bakery products. These bioactive compounds include molecules such as polyphenols (flavonoids, anthocyanins, tannins, and so on) that have shown antioxidant capacity. Dietary fiber is considered to be a bioactive compound due to its prebiotic role. It has been established that the amount of antioxidant compounds that are present inside a dietary fiber matrix are named antioxidant dietary fiber (Saura-Calixto 2011). Unripe fruits and legumes contain dietary fiber and RS, which show physiological effects due to the low content of available starch (Bello-Pérez and others 2007; Ambigaipalan and others 2011; Thompson and others 2011). Dietary fiber and resistant starch are a fermentable substrate in the colon, their fermentation products (short-chain fatty acids) resulting in diverse beneficial effects,

decreasing cholesterol levels in the bloodstream and becoming an energy source for colonocites (Serrano and Goñi 2004; Englyst and others 2005, 2007). In Mexico and some countries of Central America, maize is the most consumed cereal, and is used to make tortillas, the main staple in which the maize is used in those countries. Some scientific efforts have focused on the use of ingredients that reduce the digestibility of starch from corn and increase the consumption of indigestible carbohydrates, to produce healthier tortillas.

Use of fruit flours

Chemical composition

Diverse bakery products such as cookies and bread have been prepared with unconventional flours using different substitution levels (Table 36.1). In general, cookies have low humidity content, which can increase or remain similar compared with a control product (usually made with wheat flour) depending on the unconventional flour source. Breads have a higher moisture content which depends of the bread type and the source of the unconventional flour. Bread produced with green banana flour at different substitution levels had a similar moisture content compared with its control (Pacheco and Testa 2005); however, bread made with 100% unripe banana flour showed an increase of 100% in moisture content compared with the control sample made with wheat flour (Juárez-García and others 2006). Bakery products made with mango and orange bagasse flours showed the highest ash content (Table 36.1). Other components present in the formulation, such as minerals, can contribute to the ash content; the mineral composition of fruits is recognized by the presence of potassium, magnesium, and calcium. The level of minerals that are present in the bakery products depend of the type of flour used in the formulation, as well the ingredients used. These minerals make up an important fraction of the nutritional requirements in diet.

Table 36.1 Chemical composition of bakery products with added fruit starch or flour (g/100 g)

Sample[a]		Chemical composition				Reference
		Moisture	Ash	Protein	Fat	
Cookies	Control	3.8 ± 0.1	0.6 ± 0.1	9.5 ± 0.3	6.9 ± 0.4	Agama-Acevedo and others 2012
	15-UPF	4.7 ± 0.2	0.9 ± 0.1	9.5 ± 0.3	6.7 ± 0.7	
	30-UPF	6.0 ± 0.3	0.8 ± 0.1	8.6 ± 0.0	5.4 ± 0.5	
	50-UPF	6.4 ± 0.2	0.9 ± 0.1	7.5 ± 0.0	4.0 ± 0.9	
	25-UPF	0.9 ± 0.3	2.0 ± 0.0	7.3 ± 0.0	15.7 ± 0.0	Utrilla-Coello and others 2011
	Control	4.4 ± 0.3	0.3 ± 0.1	11.9 ± 0.4	12.6 ± 0.3	Aparicio-Saguilán and others 2007
	85-RSRP	5.7 ± 0.2	0.5 ± 0.1	5.0 ± 0.2	12.7 ± 0.0	
	Control	2.8 ± 0.0	1.5 ± 0.1	7.6 ± 0.2	18.8 ± 0.2	Fasolin and others 2007
	22.3-GBF	2.7 ± 0.0	1.6 ± 0.0	6.7 ± 0.0	19.1 ± 0.7	

	Sample					Reference
	44.6-GBF	2.8 ± 0.0	1.7 ± 0.2	6.9 ± 0.1	19.0 ± 1.7	
	66.9-GBF	2.6 ± 0.1	1.9 ± 0.0	7.8 ± 0.2	19.7 ± 0.4	
	Control	12.0 ± 0.1	4.3 ± 0.0	9.1 ± 0.1	13.8 ± 0.1	Vergara-Valencia and others 2007
	75-MDF	11.9 ± 0.0	4.3 ± 0.0	8.3 ± 0.0	13.0 ± 0.3	
	15.41-UPS	4.8 ± 0.1	1.2 ± 0.1	9.1 ± 0.1	26.9 ± 0.4	Bello-Pérez and others 2004
	17.56-UPS	2.0 ± 0.1	0.9 ± 0.1	6.1 ± 0.1	28.3 ± 0.8	
	Control	4.9 ± 0.0	2.4 ± 0.0	8.9 ± 0.1	13.2 ± 0.0	Maldonado and Pacheco 2000
	7-GBF	2.7 ± 0.6	2.7 ± 0.0	9.6 ± 0.0	13.2 ± 0.1	
Bread	Control	35.2 ± 0.1	2.2 ± 0.0	9.7 ± 0.0	15.5 ± 0.0	
	10-DFROBP	28.4 ± 0.4	2.5 ± 0.0	9.1 ± 0.0	15.5 ± 0.1	Romero-López and others 2011
	15-DFROBP	27.9 ± 0.2	3.7 ± 0.0	8.9 ± 0.1	15.3 ± 0.3	
	Control	31.5 ± 0.9	3.2 ± 0.0	11.4 ± 0.1	16.2 ± 0.2	Vergara-Valencia and others 2007
	40-MDF	26.0 ± 0.1	3.9 ± 0.0	10.2 ± 0.2	11.2 ± 0.1	
	Control	13.7 ± 0.0	2.0 ± 0.0	4.1 ± 0.0	18.4 ± 0.0	Juárez-García and others 2006
	100-UPF	26.6 ± 0.8	3.3 ± 0.0	9.8 ± 0.0	13.2 ± 0.9	
	Control	12.1	2.0 ± 0.0	16.3 ± 0.8	2.3 ± 0.0	Pacheco and Testa 2005
	7-GBF	12.6	2.1 ± 0.0	16.2 ± 0.9	2.3 ± 0.0	
	10-GBF	12.7	2.2 ± 0.0	15.8 ± 0.7	2.4 ± 0.0	
	20-GBF	12.8	2.3 ± 0.0	14.4 ± 0.9	2.3 ± 0.0	

[a]UPF, unripe plantain flour; RSRP, resistant starch-rich powder; GBF, green banana flour; UPS, unripe plantain starch.; DFROBP, dietary fiber-rich orange bagasse product; MDF, mango dietary fiber. The numbers in the sample correspond to substitution level.

When fruits flours are used in bakery products, the protein content is lower than in wheat-based products. The level of substitution of green banana flour showed a slight effect in the protein content, due to the low amount used in the formulation of the bread (Pacheco and Testa 2005). Fat is an important component in bakery products, with a wide variation of quantities depending on the product type and formulation. The addition of fruit flours which have low amounts of fat become good sources for products marked as low-fat products due to a dilution effect by the unconventional flour.

Dietary fiber and indigestible fraction

Dietary fiber and indigestible fraction (IF) constitute non-starch polysaccharides (NSP) that are not digested in the human small intestine, and undergo partial or complete fermentation in the large bowel. Dietary fiber and IF of bakery products with added fruit starch or flour are shown in Table 36.2. Cookies with added mango flour showed an increase in dietary fiber content of approximately 40% (Vergara-Valencia and others 2007), and cookies with added green banana flour had a slight increase in dietary fiber (Pacheco and Testa 2005). Modified banana starch has been used as a functional ingredient in cookies; the addition of this ingredient increased the IF around 50% compare with the control cookie made with 100% wheat flour. The IF presents a higher amount of insoluble indigestible fraction (IIF) than soluble indigestible fraction (SIF). IFF is composed mainly of resistant starch (RS), NSP, resistant protein and polyphenolic compounds. The cookie with the added modified banana starch contained a high amount of RS due to the characteristics of this ingredient (Aparicio-Saguilán and others 2007).

Table 36.2 Indigestible carbohydrates content of bakery products with added fruit starch or flour (g/100 g)

Sample[b]		Indigestible carbohydrates[a]				Reference
		TDF	TIF	IIF	SIF	
Cookies	25-UPF	7.0 ± 0.3	36.9 ± 0.8	19.7 ± 1.0	17.1 ± 0.7	Utrilla-Coello and others 2011
	Control	—	16.8 ± 0.9	13.4 ± 1.5	3.4 ± 0.2	Aparicio-Saguilan and others 2007
	85-RSRP	—	23.4 ± 0.7	20.5 ± 1.0	2.9 ± 0.1	
	Control	13.3 ± 0.1	—	—	—	Vergara-Valencia and others 2007
	75-MDF	17.4 ± 0.1	—	—	—	
	Control	4.9 ± 0.0	—	—	—	Maldonado and Pacheco, 2000
	7-GBF	5.4 ± 0.2	—	—	—	
Bread	Control	9.2 ± 0.2	20.0 ± 0.2	14.3 ± 0.3	5.7 ± 0.0	Romero-López and others 2011
	10-DFROBP	12.9 ± 0.4	25.2 ± 0.3	17.6 ± 0.2	7.6 ± 0.2	
	15-DFROBP	2.0 ± 0.3	27.4 ± 0.2	18.6 ± 0.2	8.8 ± 0.2	
	Control	14.2 ± 0.1	—	—	—	Vergara-Valencia and others 2007
	40-MDF	16.6 ± 0.1	—	—	—	
	Control	2.3 ± 0.0	18.4 ± 0.7	12.4 ± 0.5	5.9 ± 0.2	Juárez-García and others 2006
	100-UPF	5.1 ± 0.1	26.1 ± 0.9	22.3 ± 0.8	3.8 ± 0.1	
	Control	3.8 ± 0.0	—	—	—	Pacheco and Testa 2005
	7-GBF	4.5 ± 0.0	—	—	—	
	10-GBF	4.3 ± 0.0	—	—	—	
	20-GBF	4.7 ± 0.0	—	—	—	

[a]TDF, total dietary fiber; TIF, total indigestible fraction; IIF, insoluble indigestible fraction; SIF, soluble indigestible fraction.

[b]UPF, unripe plantain flour; RSRP, resistant starch-rich powder; MDF, mango dietary fiber; GBF, green banana flour; DFROBP, dietary fiber-rich orange bagasse product. The numbers in the sample correspond to substitution level.

The addition of 10 and 15% orange bagasse flour to traditional muffins increased the dietary fiber content between 40 and 60%, and a higher level of IF was determined in this bakery

product (Romero-López and others 2011). The IIF in muffins with added orange bagasse flour was higher than SIF; however, the SIF level can be considered high compared with its control and with bread supplemented with unripe banana flour. This pattern is due to the pectin present in orange bagasse that is included in the SIF content.

The addition of mango flour (40%) to wheat bread presented a slight increase in dietary fiber content compared with the control sample. A higher increase in dietary fiber level was found in unripe banana flour bread, compared with the control, and the difference between dietary fiber and IF was also very high in both breads (control bread and that made with unripe banana flour), showing higher amount of IIF in bread of unripe banana flour than control bread, as well as an inverse pattern was found for SIF (Juárez-García and others 2006). These results show that diverse indigestible compounds that are not determined in dietary fiber are quantified in the IF, perhaps resistant protein, RS, and other components are present in bread, a topic that warrants future investigation. The addition of green banana flour to the formulation of bread showed a slight increase in dietary fiber content; this could be considered to be an important feature in the development of functional bread.

Starch digestibility

Unconventional flour from fruits is used to decrease the starch digestibility of traditional bakery products. The total starch (TS) content of cookies, which was lower than that of wheat bread, is shown in Table 36.3. Different results have been found when unripe banana flour is used as an ingredient in cookies; some results show an increase in the TS content due to the high level of this polysaccharide, but when the green banana flour level increased in the formulation, a decrease in the TS content was found (Fasolin and others 2007). A similar pattern was found in bread supplemented with banana flour; when the amount of the flour increased in the formulation, TS content increased (Pacheco and Testa 2005; Juárez-García and others 2006). The addition of flour prepared with orange bagasse decreased the TS content in the bread due to the low amount of starch present in this flour; this could be a dilution effect (Romero-López and others 2011). The potential available starch (AS) is an important component in bakery products due to its impact on the glycemic response after consumption. In general, the AS content in a bakery product depends on the TS content present in the unconventional fruit flour and its substitution level. When a higher AS content was determined in bread and cookies, it was found that the glycemic response was higher in bread. The AS values presented in Table 36.3 should treated with caution because they were calculated by difference. In the digestion processes, the starch present in bread products may or may not be digested at different rates due to the presence of other components, for example dietary fiber, that increase the viscosity and decrease or avoid the contact with the enzymes that hydrolyze the starch.

Table 36.3 Carbohydrate digestibility of bakery products with added fruit starch or flour (g/100 g)

Sample[b]		Carbohydrates digestibility[a]			Reference
		TS	AS	RS	
Cookies	Control	52.3 ± 1.7	49.9[c]	2.3 ± 0.1	Agama-Acevedo and others 2012
	15-UPF	58.1 ± 0.7	54.9[c]	3.1 ± 0.2	

	30-UPF	60.8 ± 0.7	56.1[c]	5.4 ± 0.2	
	50-UPF	66.5 ± 0.7	58.1[c]	8.3 ± 0.6	
	25-UPF	60.2 ± 0.2	56.1[c]	4.1 ± 0.4	Utrilla-Coello and others 2011
	Control	—	37.2 ± 0.4	1.4 ± 0.0	Aparicio-Saguilan and others 2007
	85-RSRP	—	40.1 ± 0.6	8.4 ± 0.3	
	Control	45.8 ± 0.1	—	—	Fasolin and others 2007
	22.3-GBF	44.2 ± 0.1	—	—	
	44.6-GBF	43.3 ± 0.1	—	—	
	66.9-GBF	39.9 ± 0.2	—	—	
	Control	48.9 ± 0.9	44.1 ± 0.1	4.8[c]	Vergara-Valencia and others 2007
	75-MDF	45.5 ± 0.8	41.1 ± 0.2	4.4[c]	
	15.41-UPS	—	50.5 ± 1.3	3.2 ± 0.3	Bello-Pérez and others 2004
	17.56-UPS	—	51.0 ± 0.9	4.9 ± 0.5	
	Control	68.1 ± 0.4	67.9[c]	0.2 ± 0.0	Maldonado and Pacheco 2000
	7-GBF	67.7 ± 0.3	67.5[c]	0.2 ± 0.1	
Bread	Control	75.0 ± 0.7	65.5[c]	9.5 ± 0.5	Romero-López and others 2011
	10-DFROBP	70.2 ± 0.8	66.3[c]	3.9 ± 0.3	
	15-DFROBP	69.6 ± 0.6	67.6[c]	2.0 ± 0.3	
	Control	67.2 ± 0.4	60.9 ± 1.0	6.3[c]	Vergara-Valencia and others 2007
	40-MDF	48.4 ± 0.7	41.1 ± 0.5	7.3[c]	
	Control	59.4 ± 0.1	59.1 ± 0.1	1.0 ± 0.0	Juárez-García and others 2006
	100-UPF	63.1 ± 0.4	54.9 ± 0.1	6.7 ± 0.0	
	Control	64.2 ± 1.2	64[c]	0.2 ± 0.0	Pacheco and Testa 2005
	7-GBF	64.9 ± 0.0	64.2[c]	0.7 ± 0.0	
	10-GBF	65.5 ± 1.3	64.4[c]	1.1 ± 0.0	
	20-GBF	66.7 ± 1.4	64.4[c]	2.3 ± 0.0	

[a]TS, total starch; AS, available starch; RS, resistant starch.

[b]UPF, unripe plantain flour; RSRP, resistant starch-rich powder; GBF, green banana flour; UPS, unripe plantain starch; DFROBP, dietary fiber-rich orange bagasse product; MDF, mango dietary fiber. The numbers in the sample correspond to substitution level.

[c]Values were determinate by difference.

Starch hydrolysis percentage at different times is used to determine the rate at which starch is hydrolyzed by digestive enzymes. Grandfelt's method is a semi-*in vitro* test to determine the hydrolysis percentage; volunteers chew the food to start the starch hydrolysis by salivary α-amylase, and thereafter diverse enzymes are used to continue the hydrolysis, with a dialysis finally carried out to simulate the absorption of small sugars in the small intestine. Cookies

with added diverse fruit flours have shown lower hydrolysis percentages than a control reference (white bread) (Figure 36.1). A gradual liberation of carbohydrates with time is observed, indicating that the matrix of the product presents a physical barrier that slows down the hydrolysis of the starch by digestive enzymes. The hydrolysis index (HI) is commonly used to predict the glycemic index (pGI) (Table 36.4). Cookies supplemented with 25% of unripe plantain flour (UPF) showed a low pGI value (Utrilla-Coello and others 2011), and cookies substituted with 40% mango dietary fibre had lower pGI (55.5) than the control sample (69.5) (Vergara-Valencia and others 2007). A similar pattern was found in cookies with 85% of resistant starch-rich powder prepared from plantain starch added (Aparicio-Saguilan and others 2007). Grandfelt's test was used to determine pGI in bread prepared with different contents of fruit flours or starch; bread formulated with 100% of UPF had a pGI value of 64.3 compared with 78.8% for the control sample (Juarez-Garcia and others 2006), which indicates that the hydrolysis of starch in bread with UPF is lower due to the presence of indigestible carbohydrates such as RS or NSP that increase the viscosity of the medium, avoiding or retarding the starch hydrolysis by digestive enzymes.
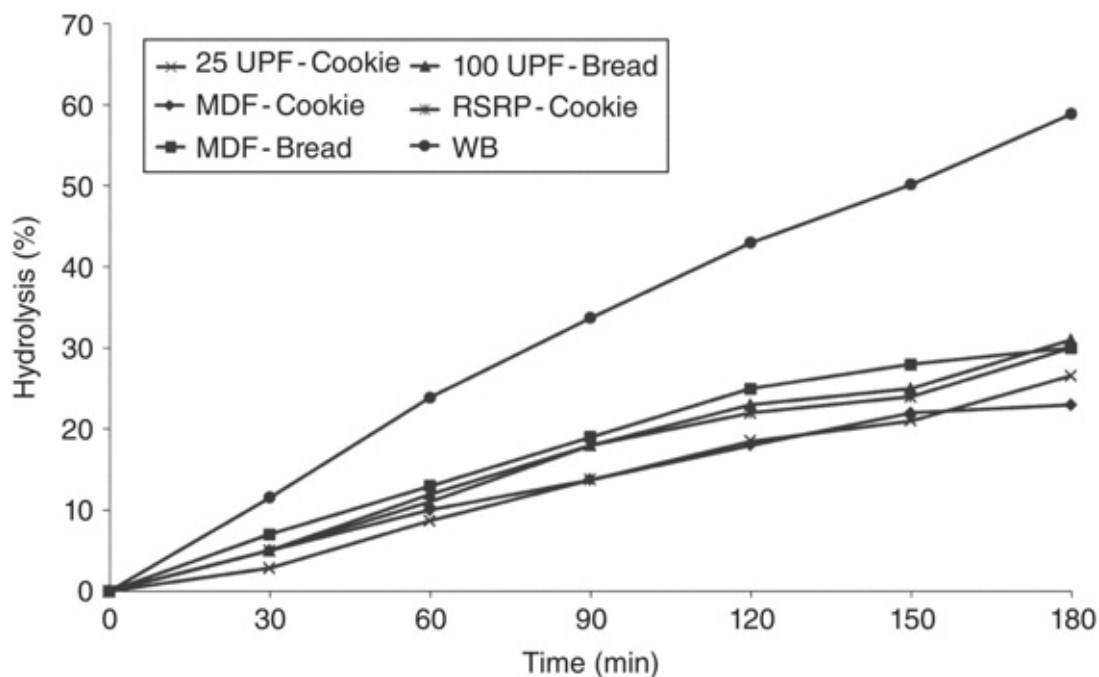
Figure 36.1 *In vitro* hydrolysis of bakery products supplemented with fruit flour: unripe plantain flour cookie (25UPF-Cookie; Utrilla-Coello and others 2011); mango dietary flour cookie and bread (MDF-Cookie and MDF-Bread, respectively; Vergara-Valencia and others 2008); unripe plantain bread (100UPF-Bread; Juárez-García and others 2007); resistant starch-rich powder cookie (RSRP-Cookie; Aparicio-Saguilan and others 2007) and white bread (WB, Utrilla-Coello and others 2011). Starch hydrolysis index (HI) of products "as eaten" (chewing/dialysis test) was assessed with the protocol developed by Granfeldt and others (1992).

Table 36.4 Hydrolysis and predicted glycemic index of bakery products with added fruit starch or flour[a]

Sample		HI	pGI	Method	Reference
Cookies	Control	—	116.8	Holm and others 1985	Agama-Acevedo and others 2012[b]
	15-UPF	—	115.2		
	30-UPF	—	106.5		
	50-UPF	—	98.6		
	25-UPF	39.9 ± 2.0	54.4	Grandfelt and others 1992	Utrilla-Coello and others 2011[c]
	Control	71.2 ± 1.0	69.5	Grandfelt and others 1992	Vergara-Valencia and others 2008[c]
	40-MDF	54.9 ± 0.8	55.5		
	Control	80.5 ± 2.6	77.6	Grandfelt and others 1992	Aparicio-Saguilan and others 2007[c]
	85-RSRP	60.7 ± 2.2	60.5		
Bread	Control	52.7 ± 0.3	81.5	Holm and others 1985	Romero-López and others 2011[b]
	10-DFROBP	45.6 ± 0.3	75.8		
	15-DFROBP	38.9 ± 0.4	70.4		
	Control	80.5 ± 2.2	77.6	Grandfelt and others 1992	Vergara-Valencia and others 2008[c]
	40-MDF	54.9 ± 0.8	55.5		
	Control	81.9 ± 3.2	78.8	Grandfelt and others 1992	Juárez-García and others 2007[c]
	100-UPF	65.1 ± 2.4	64.3		

[a]HI, hydrolysis index; pGI, predicted glycemic index. UPF, unripe plantain flour; MDF, mango dietary fiber; RSRP, resistant starch-rich powder; DFROBP, dietary fiber-rich orange bagasse product. The numbers in the sample correspond to substitution level.

[b]Predicted glycemic index (pGI) calculated from the equation proposed by Goñi and others (1997) GI = 39.21+ 0.803(H_{90}).

[c]Predicted glycemic index = 0.862 HI + 8.198 (Granfeldt 1994).

A similar pattern was found in bread substituted with mango dietary fiber, with a pGI value of 77.6% for control bread and of 55.5 for bread made with mango dietary fiber (Vergara-Valencia and others 2007). Holm's method is also used to determine the hydrolysis percentage of starch in bakery products containing fruit flours or starch (Figure 36.2). Higher

values of hydrolysis have been found using Holm's method, in which we found higher pGI values compared with Grandfelt's method ([Table 36.4](#)). The pGI value of cookies substituted with UPF decreased when the level of this flour increased in the product; however, pGI values are considered high (Agama-Acevedo and others 2012). A similar pattern was determined in bread substituted with flour of orange bagasse; the addition of this flour at two different levels decreased the pGI value (75.8 and 70.4) compared with the control bread (81.5) (Romero-López and others 2011).
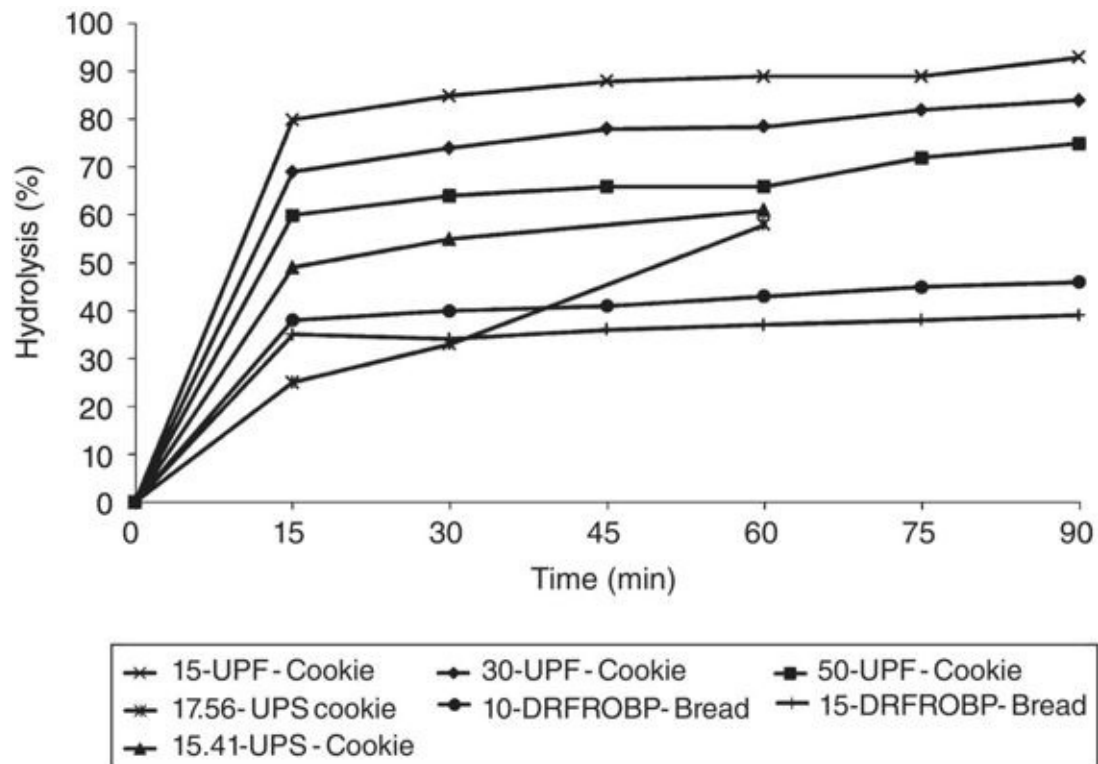
Figure 36.2 *In vitro* hydrolysis of bakery products supplemented with fruit flour: unripe plantain flour cookie (15, 30 and 50 UPF-Cookie; Agama-Acevedo and others 2012) dietary fiber-rich orange bagasse product bread (10 and 15 DRFROBP; Romero-López and others 2011); unripe plantain starch (15.41 and 17.56 UPS-Cookie; Bello-Pérez and others 2004). The *in vitro* rate of hydrolysis was measured according to Holm and others (1992).

Bioactive compounds

Bioactive compounds have been considered as an important part of a healthy diet. Bakery products made with ingredients that supply antioxidant compounds can be attractive to consumers. Very few studies have evaluated the phenolic compounds present in bakery products elaborated with unconventional and fruit flours. The phenolic compounds found in bread substituted with peel fruit flour at different levels is shown in [Table 36.5](#). Bread with added cupuassu peel flour showed a slight increase in the phenolic compounds when the level of this unconventional flour increased in the formulation. Different patterns have been reported in breads with added grape peel flour; bread with grape peel flour added at 10 g/100 g of wheat flour had a total phenolic content that was 300% higher than bread with grape peel flour added at 2.5 g/100 g of wheat flour. Grape is considered an important source of antioxidant compounds and its peel contains high amounts of them, which is why this product can be exploited as an ingredient in bakery products.

Table 36.5 Antioxidant capacity and total phenolic compounds of bread with added fruit flour (g/100 g)

Sample[a]	Phenolics compounds	Units/method[b]	Antioxidant capacity	Units/method[c]	Reference
40-MDF	10.1 ± 0.5	mg/g- Folin-Ciocalteau	8.6 ± 0.3	Antiradical efficiency, DPPH	Vergara-Valencia and others 2008
Control	540 ± 2.0	mg GAE/g-Folin-Ciocalteau	250 ± 32.0	IC50 in mg-DPPH	Ajila and others 2008
5-MPP	1800 ± 32.0		166 ± 0.2		
7.5-MPP	2250 ± 10.0		16 ± 1.8		
10-MPP	2630 ± 40.0		10 ± 0.5		
15-MPP	4350 ± 80.0		4.9 ± 0.2		
20-MPP	4500 ± 50.0		4.3 ± 0.3		
Control	3.3 ± 0.1	mg/g Folin-Ciocalteu	—		Mastrodi and others 2011
3-CPF	3.5 ± 0.1		—		
6-CPF	3.8 ± 0.0		—		
9-CPF	3.9 ± 0.1		—		
Control	0.1 ± 0.0	mg tannic acid/g Folin-Ciocalteu	—	—	Hoye and Ross 2011
2.5-GSF	1.1 ± 0.1		—		
5-GSF	2.0 ± 0.1		—		
7.5-GSF	3.0 ± 0.1		—		
10-GSF	4.3 ± 0.1		—		
Control	0.05 ± 0.0	g CE/mg	1.2 ± 0.0	TEAC-mg Trolox/g-ABTS	Korus and others 2012
5DS-BC	0.1 ± 0.0		1.3 ± 0.1		
10DS-BC	0.1 ± 0.0		1.6 ± 0.1		
15-DS-BC	0.1 ± 0-0		2.0 ± 0.1		
5DS-ST	0.3 ± 0.0		3.1 ± 0.0		
10DS-ST	0.4 ± 0.0		4.4 ± 0.1		
15DS-ST	0.7 ± 0.0		5.6 ± 0.1		

[a]MDF, mango dietary fiber; MPP, mango peel powder; CPF, cupuassu peel flour; GSF, grape seed flour; DS-BC, defatted blackcurrant seed; DS-ST, defatted strawberry seed. The numbers in the sample correspond to substitution level.

[b]GAE, gallic acid equivalents; CE, catechin equivalents.

[c]DPPH, 2,2-diphenyl-1-picrylhydrazyl; IC50, half-inhibition concentration value; TEAC, trolox equivalent antioxidant capacity; ABTS, 2,2′-azino-bis[3-ethylbenzthiazoline-6-sulphonic acid.

The antioxidant capacity of some bread mixed with unconventional flours has been measured by different methods and differences have been observed (Table 36.5). Bread with added mango peel powder had lower IC50 values when the level of this powder increased in the

product. The IC50 value indicates the least amount of sample required to obtain the same scavenging activity (Ajila and others 2008); as an example, the antioxidant capacity of certain berries is well known, so when defatted blackcurrant flour and defatted strawberry flour were added to a bread, the antioxidant capacity increases, with a higher effect for the defatted blackcurrant flour (Korus and others 2012).

Sensorial characteristics

The development of new products requires the measurement of some of their attributes, which will help to indicate their acceptability to consumers. The evaluation of bakery products using a hedonic scale with diverse attributes has been reported (Table 36.6). Cookies with added UPF showed a general acceptability (6.0), which was lower than the control sample (7.5). A similar pattern was found in cookies with added mango peel powder, as the general acceptability decreased when the substitution level of this powder in the product increased; however, the panelists could not distinguish between the control cookie and those with low amounts of mango peel powder. Similar behavior was found in the evaluation of the color, flavor, and texture parameters (Ajila and others 2008). The panelists distinguished between the cookie with added green banana flour at different levels and the control sample (Fasolin and others 2007). In other studies, a higher substitution in the formulation resulted in an important decrease in the general acceptability, for example in bread substituted with 15% orange bagasse flour (Romero-López and others 2011). As well as panelist acceptance, the degree of substitution of unconventional flours can also change the odor, color, flavor, and texture; for example, these parameters decreased when the level of cupuassu flour was increased in bread (Mastrodi and others 2011) and a similar pattern was reported in bread with added pomace apple flour (Sudha and others 2007). An inverse pattern was found in bread with added inner skin flour of watermelon in which color, flavor, and texture increased according to the level of substitution in the product; however, no control sample was used for comparison (Guimaráes and others 2010).

Table 36.6 Sensory evaluation of bakery products with added fruit flour (g/100 g)

Sample[a]		Odor	Color	Flavor	Texture	General acceptability	Hedonic scale	Reference
Cookies	Commercial bar	—	—	—	—	7.5 ± 0.1	9-points	Utrilla-Coello and others 2011
	25-UPF	—	—	—	—	6.0 ± 0.1		
	Control	—	8.7 ± 0.2	8.6 ± 0.2	8.7 ± 0.2	8.6 ± 0.1	9-points	Ajila and others 2008
	5-MPP	—	8.3 ± 0.4	8.5 ± 0.2	8.5 ± 0.4	8.4 ± 0.1		
	7.5-MPP	—	8.1 ± 0.4	8.3 ± 0.3	8.3 ± 0.4	8.2 ± 0.1		
	10-MPP	—	7.8 ± 0.4	8.3 ± 0.3	8.2 ± 0.2	8.1 ± 0.2		
	15-MPP	—	7.4 ± 0.4	7.8 ± 0.4	7.7 ± 0.2	7.5 ± 0.1		
	20-MPP	—	6.7 ± 0.5	6.9 ± 0.2	6.8 ± 0.2	6.6 ± 0.2		
	Control	—	—	—	—	7.1 ± 1.2	9-points	Fasolin and others 2007
	22.3-GBF	—	—	—	—	6.7 ± 1.2		
	44.6-GBF	—	—	—	—	7.1 ± 0.9		
	66.9-GBF	—	—	—	—	7.0 ± 1.1		
Bread	Control	—	—	—	—	6.3 ± 0.1	9-points	Romero-López and others 2011
	10-DFROBP	—	—	—	—	6.0 ± 0.2		
	15-DFROBP	—	—	—	—	4.2 ± 0.2		
	Control	7.6	7.4	7.7	7.5	—	9-points	Mastrodi and others 2011
	3-CPF	7.3	7.1	7.5	7.2	—		
	6-CPF	7.1	7.3	7.3	7.1	—		
	9-CPF	6.7	6.7	6.0	6.5	—		
	7-WISF	—	4.5	3.9	3.7	—	9-points	Guimares and others 2010
	30-WISF	—	5.9	5.9	5.0	—		
	Control	—	4.5		4.5	4.5	5-points	Sudha and others 2006
	10-AP	—	4.0		4.5	4.0		
	20-AP	—	3.5		4.0	4.0		
	30-AP	—	3.0		3.0	3.0		

[a]UPF, unripe plantain flour; MPP, mango peel powder; GBF, green banana flour; DFROBP, dietary fiber-rich orange bagasse product; CPF, cupuassu peel flour; WISF, watermelon inner skin flour; AP, apple pomace. The numbers in the sample correspond to substitution level.

Use of legume flours

Chemical composition

The moisture content of bakery products varies widely according to the starch source; cookies with added legume flours present lower values compared with bread, which could be related to the formulation of the product (Table 36.7). Legumes are characterized by the presence of minerals such as sodium and potassium in their composition, which contributes to the ash content. Cookies with added cowpea and common bean flours yielded a similar ash content (between 0.8 and 1.6%). However, control cookies showed an ash content of 2.6% and the value increased with the addition of a blend of pigeon pea and cocoyam flours in the formulation at different levels (Okpala and Chinyelu 2011). Bread with added legume flours had an ash content between 1.2 and 2.9%; the ash content presented slight variation according to the legume type for this component. Legumes are an important source of protein. Depending on the substitution level in the formulation of food products, the protein content can increase, sometimes by more than 100% compared with the control sample, as reported for cookies with added common bean flour (Medina 2006) and bread with added soy flour (Ayo and others 2007). Some bakery products with added legume flours showed a high fat content; this parameter depends of the formulation, because bread with 10% of soy flour added had a fat content of 20% (Ayo and others 2007), while another bread type with the same level of added soy flour had a fat content of 6.8% (Dhingra and Jood 2001). The fat content in bakery products is important due to the caloric supply by this component.

Table 36.7 Chemical composition of bakery products with added pulses flour (g/100 g)[a]

Sample		Chemical composition					Reference
		Moisture	Ash	Protein	Fat	TDF	
Cookies	Control	7.5 %	2.6 %	9.7 %	5.6 %	2.4 %	Okpala and others 2011
	PPF:CYF						
	20:80	6.3 %	3.2 %	10.9 %	5.3 %	2.2 %	
	30:70	6.4 %	3.4 %	11.1 %	5.6 %	2.5 %	
	40:60	6.6 %	3.5 %	11.3 %	5.8 %	2.6 %	
	50:50	6.8 %	3.6 %	11.4 %	5.8 %	2.7 %	
	60:40	6.8 %	3.7 %	11.6 %	6.0 %	2.9 %	
	30-CPF	0.9 ± 0.0	1.1 ± 0.0	10.1 ± 0.6	41.6 ± 0.2	—	Granito and others 2010
	30-FCPF	1.5 ± 0.0	1.0 ± 0.0	10.3 ± 0.3	37.6 ± 0.6	—	
	Control	5.0 ± 0.3	0.8 ± 0.2	3.4 ± 0.5	—	6.5 ± 1.1	Medina 2006
	18-CBF	5.3 ± 0.5	1.2 ± 0.2	7.3 ± 0.6	5.9 %	9.8 ± 1.6	

	20-CBF	8.2 ± 0.1	1.4 ± 0.1	7.4 ± 0.7	6.2 %	10.5 ± 0.5	
	25-CBF	8.5 ± 0.3	1.6 ± 0.4	7.5 ± 0.1	4.5 %	11.6 ± 0.5	
	30-CBF	10.8 ± 0.0	1.4 ± 0.4	8.1 ± 0.7	3.9 %	12.6 ± 0.3	
Bread	20-CBF	28.0 ± 0.2	1.9 ± 0.1	12.1 ± 0.4	18.9 ± 0.7	—	Granito and others 2010
	20-FCBF	19.2 ± 0.8	1.6 ± 0.5	13.0 ± 1.2	19.6 ± 0.0	—	
	30-PPF	12.7 ± 0.2	1.3 ± 0.1	10.7 ± 0.2	23.5 ± 1.0	—	
	30-FPPF	7.3 ± 0.3	1.2 ± 0.1	10.0 ± 0.8	22.8 ± 1.3	—	
	Control	20.0 ± 0.0	2.0 ± 0.0	12.9 ± 0.0	14.2 ± 0.1	3.6 ± 0.0	Utrilla-Coello and others 2007
	20-CF	20.4 ± 0.2	2.3 ± 0.2	14.2 ± 0.1	14.9 ± 0.1	7.4 ± 0.2	
	40-CF	20.3 ± 0.2	2.5 ± 0.1	15.9 ± 0.2	14.4 ± 0.4	8.5 ± 0.1	
	Control	9.8 ± 1.4	2.9 ± 0.9	5.0 ± 1.4	14.8 ± 3.5	—	Ayo and others 2007
	5-SF	9.6 ± 1.7	2.9 ± 0.9	6.5 ± 1.4	15.3 ± 2.7	—	
	10-SF	9.5 ± 0.9	2.6 ± 0.4	9.9 ± 2.1	19.9 ± 2.8	—	
	15-SF	9.5 ± 0.6	2.5 ± 0.6	11.5 ± 2.2	21.9 ± 2.6	—	
	20-SF	9.4 ± 1.3	1.8 ± 0.2	12.0 ± 1.6	22.4 ± 3.1	—	
	30-SF	9.3 ± 0.8	1.6 ± 0.6	14.2 ± 1.7	24.0 ± 3.5	—	
	Control	39.5 %	—	8.0 %	3.5 %	2.9 %	Hawkins and Johnson 2005
	24.3-CF	36.3 %	—	10.0 %	4.3 %	4.5 %	
	24.3-EXCF	42.1 %	—	9.1 %	3.4 %	5.1 %	
	Control	—	2.1 ± 0.5	11.5 ± 2.0	5.4 ± 0.5	8.9 ± 0.6	Dhingra and Jood 2001
	5-SF	—	2.3 ± 0.4	12.2 ± 1.0	6.3 ± 0.4	8.8 ± 0.2	

10-SF	—	2.4 ± 0.3	13.7 ± 0.8	6.8 ± 0.6	8.5 ± 0.3	

Dietary fiber

The actual interest in increasing the consumption of indigestible carbohydrates as dietary fiber is due to the health benefits it offers. Diverse studies have shown that dietary fiber is not consumed in sufficient quantities (Hager and others 2011). Health agencies recommend the consumption of at least 25–30 g of dietary fiber per day (Mermelstein 2011). Until recently, bakery products, including those classified as gluten-free, contained low amounts of dietary fiber. Cookies with added common bean flour had a dietary fiber content between 9.8 and 12.6%, depending of the substitution level (Table 36.7). However, a blend of pigeonpea and cocoyam flours added to a cookie formulation did not show increase in dietary fiber content (2.4–2.9%). Bread with added chickpea flour showed an increase in dietary fiber content as high as 100% in bread with 40% of chickpea flour (8.5%) (Utrilla-Coello and others 2007). However, the addition of 10% of soy flour in the bread did not produce any changes in the dietary fiber content (Dhingra and Jood 2001). The search for new formulations using fiber-rich ingredients is an interesting alternative for food industry.

Starch digestibility

In general, bread with soy flour added at different levels showed similar total starch (TS) contents and no differences were found compared with the control sample (Table 36.8). The substitution with soy flour in the bread did not decrease the level of starch, as shown by the similar TS content present in wheat and soy flour (Ayo and others 2007). The addition of chickpea flour in a bread preparation at 20 and 40% w/w, decreased the TS content in the product, which indicates that a lower amount of this carbohydrate will be consumed and consequently it will provide a minor supply of glucose. Chickpea flour prepared by extrusion and used as an ingredient in bread preparation contained a lower amount of TS than the bread substituted with chickpea flour that was prepared by milling and the one prepared traditionally that was used as a control (Hawkins and Johnson 2005). The AS content decreased in the breads formulated with chickpea flour and it was higher when the substitution level of the chickpea flour increased; a lower amount of AS was determined in the bread made with chickpea flour prepared by extrusion (Hawkins and Johnson 2005). Legumes are characterized by their slowly digestible starch characteristics, determined as RS. Bread with added chickpea flour showed an important increase in RS content compared with the control sample, and the RS level increased when a higher amount of chickpea flour was added (Utrilla-Coello and others 2007). However, the chickpea flour prepared by extrusion and used for bread elaboration presented lower RS content than the chickpea flour obtained by milling (Hawkins and Johnson 2005). Extrusion of chickpea flour produces starch gelatinization that decreases the RS content in the flour.

Table 36.8 Carbohydrate digestibility of bread with added pulses flour (g/100 g)[a]

Sample	Carbohydrates digestibility			Reference
	TS	AS	RS	
Control	59.0[b]	58.3 ± 0.6	0.7 ± 0.2	Utrilla-Coello and others 2007
20-CF	57.8[b]	55.2 ± 0.6	2.6 ± 0.2	
40-CF	54.9[b]	51.7 ± 0.6	3.2 ± 0.2	Ayo and others 2007
Control	73.9 %	—	—	
5-SF	73.7 %	—	—	
10-SF	73.3 %	—	—	
15-SF	72.9 %	—	—	
20-SF	72.2 %	—	—	
30-SF	71.5 %	—	—	
Control	45.8 ± 1.3	41.4[b]	4.4 ± 1.2	Hawkins and Johnson 2005
24.3-CF	45.5 ± 3.4	39.2[b]	6.3 ± 3.0	
24.3-EXCF	39.7 ± 1.8	35.1[b]	4.6 ± 1.0	

[a]TS, total starch; AS, available starch; RS, resistant starch; CF, chickpea flour; EXCF, extruded chickpea flour; SF, soy flour. The numbers in the sample correspond to substitution level.

[b]Values were determinate by difference.

Bread elaborated with two different levels of chickpea flour showed low and slow starch hydrolysis (Figure 36.3), this resulting in low pGI values (Table 36.9) (Utrilla-Coello and others 2007). This pattern can be due to the formulation (ingredients) used in bread elaboration. This was corroborated in two bread types made with whole pea flour (WPF), because the pGI values were different in traditional bread with 100% WPF (50.3) and biscotti with 100% WPF (45.4). These pGI values were lower than those determined in bakery products made with wheat flour (75.4 and 63.9) (Marinangeli and others 2009). Bread substituted with low level of lentil flour (7%) and using the Goñi's method (Goñi and others 1997) presented pGI similar to that of control product (68.1 and 64.5, respectively) (Ferrer-Mairal and others 2011).
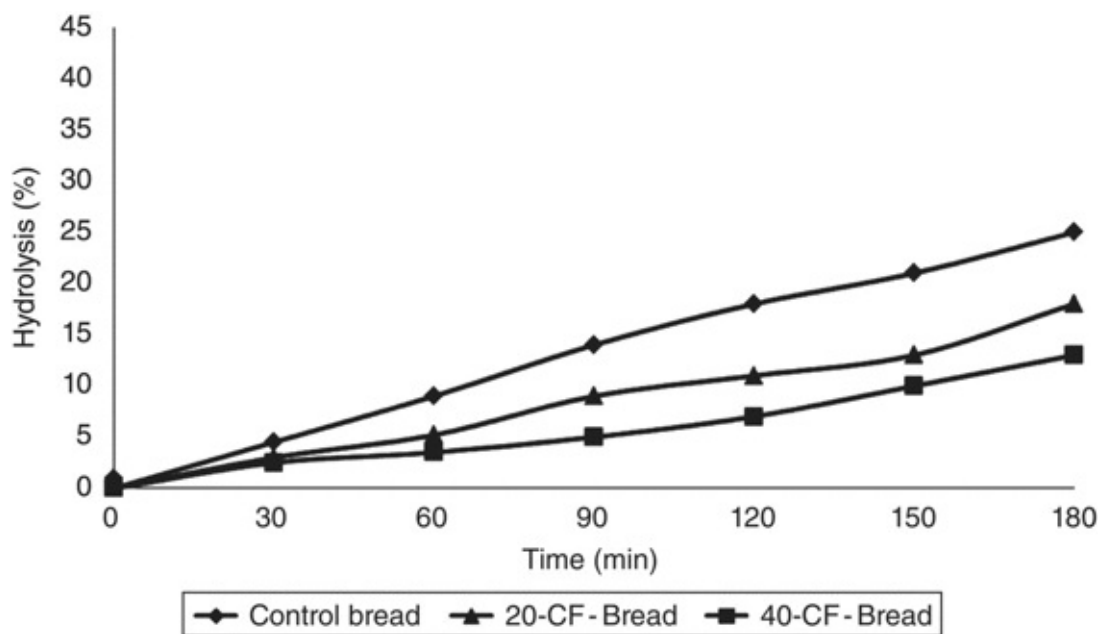
Figure 36.3 *In vitro* hydrolysis rate of bread supplemented with chickpea flour. Hydrolysis rate was assessed with the protocol developed by Granfeldt and others (1992). CF, chickpea flour. (Utrilla-Coello and others 2007).

Table 36.9 Hydrolysis and glycemic index of breads with added pulses flour[a]

Sample	HI	GI	Method	Reference
Control	69.5 ± 1.8	68.1 ± 1.6[b]	Goñi and others 1997	Ferrer-Mairal and others 2011
7-LF	65.3 ± 2.1	64.5 ± 1.8[b]		
Bread control	—	75.4 ± 14.9	Wolever and Jenkins 1986	Marinangeli and others 2009
100-WYPF	—	50.3 ± 8.0		
Biscotti control	—	63.9 ± 7.1		
100-WYPF	—	45.4 ± 8.2		
Control	66.3 ± 1.2	65.3[b]	Grandfelt and others 1992	Utrilla-Coello and others 2007
20-CF	44.9 ± 0.9	46.9[b]		
40-CF	30.7 ± 0.6	34.7[b]		

[a] HI, hydrolysis index; GI, glycemic index; LF, lentil flour; WYPF, whole yellow pea flour; CF, chickpea flour. The numbers in the sample correspond to substitution level.

[b] These values were calculated from the HI by using the formula: (pGI) predicted glycemic index = 0.862 HI + 8.198 (Granfeldt, 1994).

Bioactive compounds

The antioxidant capacity of cookies substituted with pulse flours is presented in Table 36.10. Cookies with added bean flours (pinto and navy) at different levels showed an increase in the antioxidant capacity compared with the control sample. Cookies made with 100% pulse flours showed differences between them, because the antioxidant capacity of cookies produced with 100% navy bean was 100% higher than the control sample, while for cookies made with 100% pinto bean flour, antioxidant capacity was 200% higher than the control cookie. Differences in the antioxidant capacity are due to the higher amount of anthocyanins present in pinto beans than in navy beans (Golam and others 2011). The addition of lentil flour to cookies at different levels showed similar antioxidant capacity to those cookies in which navy bean flour was added. When pulse flours have similar antioxidant capacities, which ones will be selected for addition will depend on the flavor and taste characteristics they impart and on the sensorial characteristics of the final product.

Table 36.10 Antioxidant capacity of cookies with added pulses flour (g/100 g)

Sample[a]	Antioxidant capacity	Units/method[b]	Reference
Control	98.8 ± 9.0	μmolTE/100 g Modified version of Brand-Williams and others (1995)	Zucco and others 2011
25-NBF	96.0 ± 12.0		
50-NBF	160.4 ± 24.8		
75-NBF	197.3 ± 15.8		
100-NBF	180.1 ± 28.8		
25-PBF	176.8 ± 11.6		
50-PBF	218.1 ± 23.5		
75-PBF	303.7 ± 22.9		
100-PBF	296.8 ± 17.2		
25-GLF	138.9 ± 6.9		
50-GLF	160.0 ± 16.3		
75-GLF	175.2 ± 9.3		
100-GLF	185.0 ± 29.8		

[a]NBF; navy bean fine flour; PBF, pinto bean fine flour; GLF, green lentil fine flour. The numbers in the sample correspond to substitution level.

[b]TE, trolox equivalents.

Sensorial characteristics

Bread and cookies with added pulses generally had a low acceptability when the substitution of these flours increased (Table 36.11). However, the addition of some fermented flours at the same level as their non-fermented counterpart in bread and cookies did not modify general product acceptability by consumers (Granito and others 2010). The addition of pulse flour did not change some values in the parameters evaluated in the sensorial text. It was reported that substitution (50%) of wheat flour by cowpea flour did not substantially modify the color and texture of the cookie (McWatters and others 2003); a similar pattern was found in some

values at low levels of substitution for unconventional flours (Ayo and others 2007; Medina 2006; Okpala and Chinyelu 2011). The results of sensorial attributes are important to assess the amount of unconventional flours that can be added to the products while maintaining consumer acceptablility.

Table 36.11 Sensory evaluation of bakery products with added pulses flour (g/100 g)

Sample[a]		Odor	Color	Flavor	Texture	General acceptability	Hedonic scale	Reference
Cookies	Control	—	8.0	8.2	7.9	8.3	9-points	Okpala and others 2011
	PPF:CYF							
	20:80	—	8.0	7.2	7.7	8.0		
	30:70	—	7.6	7.2	6.8	6.9		
	40:60	—	6.6	6.9	6.4	6.4		
	50:50	—	6.4	6.9	6.0	6.4		
	60:40	—	5.4	6.8	5.8	6.2		
	30-CPF	5.4 ± 1.2	6.1 ± 0.9	5.9 ± 0.9	5.4 ± 1.2	6.5 ± 0.6	7-points	Granito and others 2010
	30-FCPF	5.3 ± 1.3	6.3 ± 0.5	5.8 ± 0.9	5.3 ± 1.3	6.7 ± 0.8		
	18-CBF	3.9 ± 0.9	4.0 ± 1.0	3.8 ± 0.9	3.3 ± 1.1	2.9 ± 1.2	5-points	Medina 2006
	20-CBF	3.7 ± 1.0	3.8 ± 0.9	3.5 ± 1.1	3.4 ± 1.1	2.5 ± 1.0		
	25-CBF	3.6 ± 1.0	3.8 ± 1.0	3.4 ± 1.3	3.2 ± 1.0	2.3 ± 1.1		
	30-CBF	3.6 ± 1.1	3.5 ± 1.0	3.3 ± 1.0	3.3 ± 1.1	2.3 ± 1.1		
	Control	—	6.8	7.1	6.9	6.9	9-points	McWatters and others 2003
	50-CPF	—	7.0	4.8	6.4	5.2		
Bread	20-CBF	5.9 ± 1.4	6.3 ± 0.8	6.3 ± 0.7	5.9 ± 1.3	5.2 ± 1.0	7-points	Granito and others 2010
	20-FCBF	4.9 ± 1.6	6.1 ± 1.0	5.6 ± 1.5	4.9 ± 1.6	5.2 ± 1.7		
	30-PPF	3.9 ± 1.7	5.8 ± 1.5	5.1 ± 1.8	3.9 ± 1.7	5.1 ± 1.1		
	30-FPPF	4.9 ± 2.0	5.5 ± 1.3	6.1 ± 0.8	4.9 ± 2.0	5.2 ± 1.7		
	Control	6.4 ± 1.0	7.1 ± 1.2	6.2 ± 0.9	7.5 ± 1.7	6.1 ± 0.8	9-points	Ayo and others 2007
	5-SF	6.7 ±	6.9 ±	6.1 ±	7.2 ± 1.0	6.4 ± 0.7		

	0.8	1.0	0.6		
10-SF	7.2 ± 0.9	6.8 ± 0.9	5.9 ± 0.5	6.8 ± 0.9	6.7 ± 0.2
15-SF	7.2 ± 0.7	6.5 ± 0.0	5.0 ± 0.6	6.4 ± 0.4	6.6 ± 0.3
20-SF	5.5 ± 0.4	5.5 ± 0.6	4.2 ± 0.4	5.9 ± 0.7	4.5 ± 0.3
30-SF	4.3 ± 0.3	4.6 ± 0.4	4.1 ± 0.4	5.6 ± 0.6	4.4 ± 0.5

[a]PPF, pigeonpea flour; CYF, cocoyam flour; CPF, cowpea flour; FCPF, fermented cowpea flour; CBF, common bean flour; FCBF. Fermented common bean flour; FPPF, fermented pigeonpea flour; SF, soy flour. The numbers in the sample correspond to substitution level.

Other bakery products: tortilla

Chemical composition

Tortilla is considered the main staple for Mexican people living in Mexico and those living in the United States. Tortilla is considered a bakery product as it is made by cooking in an oven for some minutes. Traditionally, tortilla is made with corn, but in the north of Mexico wheat is also used; nowadays, although wheat tortilla is extensively consumed in Mexico, it eaten less than corn tortilla. In some regions of the country, tortilla is mixed with other unconventional ingredients. The chemical composition of corn tortilla is shown in Table 36.12. The substitution of corn with diverse unconventional flours is intended to increase the tortilla's nutritional value and to manage the special nutritional requirements of people with conditions such as diabetes and obesity. The addition of two unconventional flours – cassava and unripe banana flours – decreases the protein content in corn tortilla and slightly increases the dietary fiber content. Opposing this trend, an increase in protein and fat content was determined in corn tortilla substituted with amaranth flour (Islas-Hernández and others 2007). Prickly pear (*Opuntia ficus-indica*) consumption is recommended for people with diabetes as it contains NSPs that decrease the glucose level in the blood (Klemens 2006). The addition of prickly pear to corn tortilla showed a decrease in fat content but the total dietary fiber did not change compared with the control tortilla (Guevara-Arauza and others 2011). An important increase in protein and total dietary fiber content was found in tortilla made with quality protein maize (QPM) and with added black bean; these values can have important physiological effects during the consumption of this tortilla (Grajales-García and others 2012).

Table 36.12 Chemical composition of tortillas with added unconventional flours (g/100 g)

Sample[a]	Chemical composition					Reference
	Moisture	Ash	Protein	Fat	TDF	
Control	—	1.4 ± 0.1	7.7 ± 0.3	2.3 ± 0.2	9.8 ± 0.3	Unpublished data
50-CF	—	1.5 ± 0.1	5.2 ± 0.0	1.5 ± 0.1	10.7 ± 0.2	
40-UPF	—	1.4 ± 0.1	5.8 ± 0.1	2.5 ± 0.1	10.8 ± 0.2	
Control	7.7 ± 1.2	0.8 ± 0.1	3.8 ± 0.7	4.2 ± 0.6	5.2 ± 0.3	Guevara-Arauza and others 2011
48-NDF	12.2 ± 1.3	1.2 ± 0.1	3.3 ± 0.4	3.1 ± 0.2	4.9 ± 0.3	
QPM	—	1.7 ± 0.0	8.8 ± 0.1	4.4 ± 0.2	9.4 ± 0.3	Grajales-García and others 2011
30-BBT	—	2.6 ± 0.0	12.0 ± 0.4	3.9 ± 0.3	14.7 ± 0.3	

Control	47.6 ± 0.3	1.3 ± 0.0	9.1 ± 0.1	4.3 ± 0.0	16.5 ± 0.2	Rendon-Villalobos and others 2009a, 2009b
10-FS	43.8 ± 0.5	1.5 ± 0.0	10.8 ± 0.0	8.2 ± 0.0	19.8 ± 0.0	
15-FS	44.1 ± 0.3	1.4 ± 0.0	11.6 ± 0.3	9.9 ± 0.0	21.8 ± 0.0	
20-FS	44.1 ± 0.3	1.6 ± 0.0	12.9 ± 0.0	12.0 ± 0.1	23.5 ± 0.2	
QPM Control	—	3.8	7.2	2.5	4.9	Mora-Avilés and others 2007
22-BF + QPM	—	5.0	11.0	2.0	3.4	
RMF Control	—	4.2	8.1	2.8	4.5	
22-BF + RMF	—	2.1	13.1	2.4	2.1	
CMF Control	—	1.4	10.2	2.9	1.9	
22-BF + CMF	—	2.0	11.4	1.6	2.8	
Control	5.7 ± 9.0	1.4 ± 3.0	7.5 ± 8.0	2.0 ± 8.0	—	Islas-Hernández and others 2007
20-AF	5.5 ± 2.0	1.5 ± 1.6	10.6 ± 2.0	4.8 ± 15.0	—	
BMT	18.4 ± 0.4	2.2 ± 0.1	6.5 ± 0.5	1.7 ± 0.0	1.8 ± 0.4	Obatolu and others 2007
30-BST	17.6 ± 0.3	3.6 ± 0.0	16.4 ± 0.9	5.3 ± 0.1	1.1 ± 0.1	
FMT	12.4 ± 1.0	2.5 ± 0.1	6.4 ± 0.3	8.2 ± 0.2	1.5 ± 0.1	
30-FST	12.3 ± 0.7	3.4 ± 0.1	15.9 ± 0.7	12.2 ± 0.1	1.2 ± 0.2	
White maize	19.1 ± 0.3	1.9 ± 0.0	9.3 ± 0.1	3.0 ± 0.0	—	Hernández-Salazar and others 2006
Blue maize	13.4 ± 0.4	1.9 ± 0.0	8.3 ± 0.1	2.2 ± 0.0	—	
Maize-bean	15.3 ± 0.4	2.9 ± 0.0	10.5 ± 0.1	3.6 ± 0.1	—	

[a]CF, cassava flour; UPF, plantain flour; NDF, nopal dietary fiber; QPM, quality protein maize; BBT, black bean tortilla; FS, flaxseed; BF, bean flour; RMF, regular maize flour; CMF, commercial maize flour; AF, amaranth flour; BMT, baked maize tortilla; BST, baked soybean tortilla; FMT, fried maize tortilla; FST, fried soybean tortilla. The numbers in the sample

An increase in protein content was determined in tortilla made with QPM regular maize and commercial maize flour, with added black bean flour. A decrease in the total dietary fiber content was found when black bean was added, except in the tortilla made with commercial flour (Mora-Aviléz and others 2007). Commercial tortilla flour with a blend of maize and black bean showed a slight increase in protein content compared with tortilla made of traditionally nixtamalized white maize (Hernández-Salazar and others 2006). The addition of flaxseed flour at different levels in corn tortilla increased the fat content two to three times, as well as increasing protein and NSP (Rendón-Villalobos and others 2009). The addition of soy to maize tortilla showed an important increase in protein, fat, and ash content, but a decrease in total dietary fiber. Other processes used to make maize tortilla added with soy (baked or fried) can also affect those contents (Obatolu and others 2007).

Starch digestibility

The starch digestibility of tortilla substituted with cassava and unripe banana flour was not modified, because available (AS) and resistant (RS) starch contents similar to the control sample were found (Table 36.13). The substitution of the traditional corn tortilla with 30% black bean flour decreased the AS content and increased the RS level; tortilla with the maize–bean blend had a lower starch content and its consumption would supply a minor amount of glucose (Grajales-García and others 2012). In a commercial flour maize–bean blend, however, the RS content did not change compared with the normal maize tortilla (Hernández-Salazar and others 2006). The addition of flaxseed flour to corn tortilla showed a similar pattern to that found in tortilla with the maize–bean blend, due a decrease in AS content and an increase in RS (Rendón-Villalobos and others 2009). Tortilla substituted with 20% amaranth flour showed a decrease in AS and RS contents compared with the control tortilla (Islas-Hernández and others 2007).

Table 36.13 Carbohydrate digestibility of tortillas with added unconventional flours (g/100 g)

Sample[a]	Carbohydrates digestibility			Reference
	TS	AS	RS	
Control	78.0 ± 2.5	76.2	1.8 ± 0.5	Unpublished data
50-CF	75.7 ± 0.9	75.1	0.6 ± 0.1	
40-UPF	78.6 ± 0.7	76.0	2.6 ± 0.3	
QPM	76.7 ± 0.8	71.7 ± 0.8	5.0 ± 0.0	Grajales-García and others 2011
30-BBT	66.8 ± 0.5	60.5 ± 0.5	6.3 ± 0.0	
Control	75.4 ± 0.5	68.5 ± 0.2	1.9 ± 0.0	Rendón-Villalobos and others 2009
10-FS	67.5 ± 0.3	61.6 ± 0.8	2.8 ± 0.0	
15-FS	65.5 ± 0.4	58.1 ± 0.7	3.3 ± 0.2	
20-FS	60.2 ± 0.4	55.9 ± 1.2	5.1 ± 0.2	
Control	94.2[b]	76.2 ± 1.0	18.0 ± 1.0	Islas-Hernández and others 2007
20-AF	87.3[b]	73.3 ± 1.2	14.0 ± 1.0	
White maize	67.2 ± 1.0	63.5 ± 0.4	2.6 ± 0.4	Hernández-Salazar and others 2006
Blue maize	68.6 ± 1.1	67.5 ± 0.4	2.0 ± 0.1	
Maize-bean	65.6 ± 2.3	60.3 ± 0.7	3.0 ± 0.1	

[a]TS, total starch; AS, available starch; RS, resistant starch; CF, cassava flour; UPF, plantain flour; QPM, quality protein maize; BBT, black bean tortilla; FS, flaxseed; AF, amaranth flour. The numbers in the sample correspond to substitution level.

[b]Values were determinate by difference.

The starch digestibility data was used to obtain a predicted glycemic index (Table 36.14). The predicted glycemic index (pGI) of tortilla substituted with cassava, unripe banana, and amaranth flour was not modified compared with the control sample (Islas-Hernández and others 2007). Tortilla substituted with flaxseed and black bean flours, however, showed a decrease in pGI (Rendón-Villalobos and others 2009; Grajales-García and others 2012), indicating that the consumption of these tortillas could provide a lower amount of released glucose.

Table 36.14 Predicted glycemic index of tortillas with added unconventional flours

Sample[a]	pGI[b]	Reference
Control	102.3	Unpublished data
50-CF	102.5	
40-UPF	106.3	
QPM	87.9 ± 0.2	Grajales-García and others 2011
30-BBT	79.7 ± 0.1	
Control	101.4	Rendón-Villalobos and others 2009
10-FS	88.2	
15-FS	80.9	
20-FS	73.6	
Control	103.1	Islas-Hernández and others 2007
20-AF	107.1	

[a]CF, cassava flour; UPF, plantain flour; QPM, quality protein maize; BBT, black bean tortilla; FS, flaxseed; AF, amaranth flour. The numbers in the sample correspond to substitution level.

[b]pGI, predicted glycemic index calculated from the equation proposed by Goñi and others (1997). GI = 39.21 + 0.803(H_{90}). (Holm and others 1985).

Sensorial characteristics

Diverse sensorial studies of tortilla substituted with unconventional flours have been published (Table 36.15). In general, overall acceptance by panelists was determined in tortillas with those added flours, and differences were found in the process by which tortilla was prepared (baked and fried). These results should encourage the use of unconventional flour to make tortillas due to its acceptability by consumers.

Table 36.15 Sensory evaluation of tortillas with added unconventional flours (g/100 g)

Sample[a]	Color	Flavor	Texture	General Acceptability	Hedonic scale	Reference
Control	—	5.7 ± 1.8	6.1 ± 2.0	5.8 ± 1.7	9-points	Anton and others 2009
25-CBF	—	7.0 ± 1.4	7.4 ± 1.4	7.2 ± 1.3		
25-CBF + 0.5GG	—	7.0 ± 1.5	7.2 ± 1.3	7.0 ± 1.4		
BAKED						
UMT	7.5	5.0	6.1	4.4	9-points	Obatolu and others 2007
30-UST	5.4	6.2	6.1	4.5		
SSMT	6.9	7.0	6.0	6.1		
30-SSST	5.1	7.0	6.1	6.2		
SAMT	6.9	7.2	5.8	7.5		
30-SAST	6.3	7.8	6.4	7.8		
FRIED						
UMT	6.0	6.1	7.2	4.0		
30-UST	6.2	6.1	7.0	4.4		
SSMT	6.2	7.0	7.3	7.2		
30-SSST	6.4	7.1	7.2	7.5		
SAMT	6.2	6.5	7.5	5.7		
30-SAST	6.4	6.8	7.3	5.8		

[a]CBF, common bean flour; GG, guar gum; UMT, unsweetened maize tortilla; UST, unsweetened soy tortilla; SSMT, sugar-sweetened maize tortilla; SSST, sugar sweetened soy tortilla; SAMT, salted maize tortilla; SAST, salted soy tortilla. The numbers in the sample correspond to substitution level.

Final remarks

The interest of the food industry to produce functional products includes bakery products, which traditionally have a high digestible carbohydrate content and a negative impact on health, usually related to overweight and obesity problems, and prohibiting their consumption by diabetic patients. The use of unconventional flours derived from unripe fruits and legumes opens up new possibilities for developing functional bakery products that are acceptable to consumers and that contain a higher amount of dietary fiber and bioactive compounds than commercially available products. The reduction in the predicted glycemic index indicates that a low amount of glucose will be carried to the blood after the consumption of functional bakery products made using unconventional flours, leading to some health benefits such as a lower postprandial glucose and insulinemic response.

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37

Dietetic Bakery Products[a]

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Introduction

Increased consumer income, improved consumer understanding of the role of healthier forms of nutrition, and enhanced consumer expectations, are leading to a shift in the perception of the role of diet in individuals' lifestyle. Global health systems in developed and developing countries have begun to shift emphasis. Health system changes involve shifting from dealing with infectious disease to managing the challenges presented by increases in mortality caused by chronic diseases including cardiovascular diseases, diabetes, and cancer (Magnusson 2009). Therefore, in recent years, assessing the health consequences of food consumption habits have emerged as important topics of inquiry (Raghunathan and others 2006).

Bakery products may be usefully adapted to increase healthier eating options for consumers. 'We are what we eat' is an apt adage adopted by some consumers to inform their dietary choices. It is therefore important for bakers to also be conversant with the range of consumer preferences and dietary needs characterising the present bakery products market.

In this chapter, bakery products that cater for the special dietary needs of consumers are introduced. The following dietary market opportunities will be discussed:

- Food intolerances (specifically gluten and lactose intolerance and allergy to eggs),
- Bakery products that contribute to a healthier life-style (low-fat, low-sugar, and high fiber products),
- Bakery products required for specialized diet requirements (diabetic consumers),
- Bakery products for special religious diet requirements (Kosher and Halal),
- Bakery products suitable for lifestyle choices (sports nutrition, vegetarianism, and veganism), and
- Bakery products suitable for various stages of human development (children, women, and seniors).

In each of the above, a brief introduction is used to provide relevant information. A sample bakery recipe is modified to suit the relevant dietary requirements. These recipes are simple outlines and based on conventional bakery production methods. Ingredients in the recipes provided are presented as percentages based on flour weight (bakers' percent) and exceptions to this rule are indicated. The examples show how bakery recipes are modified for each relevant dietary requirement and help the reader understand how basic principles of recipe balance are applied towards recipe adaptation or modification. In some sections, only minor modifications in the recipes are required; in these cases, only the "model" recipes are provided.

Each section then includes a discussion on the challenges that each dietary requirement will present to the baker or bakery technologist.

Food intolerances

A food allergy is caused by an immune response to a food substance and is characterized by almost immediate allergic reactions when the food is eaten. A food intolerance, on the other hand, does not involve the immune system, and symptoms occur over a period of time and remain as long as the food the individual is intolerant to remains in their diet (Wardlaw 1993).

The main food intolerances/allergies that affect the bakery industry are intolerance to gluten or lactose or an allergy to eggs. Allergies to other food products, notably peanuts and sulfites, also affect the baking industry, but a clearcut choice to avoid using these ingredients in bakery products is possible, whereas the three ingredients in this section, wheat and other gluten bearing cereals, dairy products, and eggs, are basic ingredients used in almost all bakery products.

Gluten intolerance

Two forms of susceptibility to gluten in individual's diets are coeliac or celiac disease, an allergic response, and gluten intolerance, a non-immunological but sensitivity reaction. Coeliac disease is a "state of heightened immune response to undigested gluten in genetically susceptible people" (Phillips, 2010, p 26). Coeliac disease is also "know as gluten sensitive enteropathy or celiac sprue" (Daitch and Epperson 2011). The gluten proteins, gliadin in wheat, secalins in rye and hordeins in barley are implicated (Phillips 2010). Gluten or wheat intolerance does not involve the immune system, instead wheat intolerance occur over a longer period of time, are less severe than a food allergy and in most cases, require large amounts of food to be ingested before symptoms manifest (Mackenzie and Venter 2010). Worldwide prevalence of celiac disease is estimated to be between 0.5 to 1.0 % but the Arab population of the Western Sahara has been found to have a higher incidence of 5.6% (Phillips 2010).

Since most bakery products are wheat based, baking for gluten intolerance becomes a challenge to commercial baking operations. No contamination by cereals that carry gluten must occur during the production of gluten-free products. Besides wheat, rye, oats, and barley, the rye/wheat cross, triticale and the older forms of wheat like spelt, einkorn, and kamut should also be avoided.

Wheat flour may also be present in some ingredients used in the production of certain bakery products. The key ones to take note of are baking powder, icing sugar, commercial salad dressings including mayonnaise, condiments like curry powder, prepared mustards, tomato sauce, soy products made from fermented wheat, and dairy products such as processed cheese, commercial ice creams, and flavored yogurt (Hagman 2000).

Care must be taken not only at the recipe formulation stage but at all steps of the production of gluten-free products so that the product does not become contaminated by wheat or other gluten-bearing flour. One should ensure that all equipment used is free of gluten-bearing flour, which in commercial baking, will require the setting up of a separate production area for gluten-free products.

The gluten forming function of wheat flour is an important attribute to dough formation and

development in bread making and in the final structure in other baked products including cakes, cookies, and pastries. Therefore, gluten-free baking is presented with the challenge of replicating the functionality of gluten in the absence of wheat flour use.

In some baked products, a high level of the proteins contributing to the overall structure is provided by other ingredients such as eggs. In this case, the substitution for all of the wheat flour with a starch, usually very fine rice flour or potato starch, will produce an acceptable baked product. Examples of such baked products include sponges made using the conventional method produced by whisking eggs and sugar together and then folding in the dry ingredients, and chou paste. The "cooking off" of the flour at the beginning of the chou paste-making process removes many of the functional aspects of the flour proteins. In conventional cake and sponge making, ground nuts like walnuts, almonds, pecans, hazelnuts, Brazil nuts, peanuts, chestnuts, cashews, and coconuts may also be used to replace flour (Mauksch 1997).

A mixture of starches derived from rice, potatoes, and tapioca maybe used to replace wheat flour in the baking of gluten-free bread and cake products (Hagman 2000). The proportions of cornstarch, cassava starch, and rice flour need to be optimized so that the gluten-free bread produced meets specific volume, crumb grain, and bread score requirements (Sanchez and others 2002). The nutritive protein contribution from wheat flour is replaced by the addition of milk powder or egg whites. Crumbliness in the product is prevented by the use of gums. Xanthan gum is the preferred choice as guar gum has a laxative effect on some individuals.

Louis (2003) recommends the use of sorghum, teff, and bean flours made from garbanzo (chickpeas) and fava (broad) beans (called garfava flour) as replacements for wheat flour in baked products. Sorghum is especially ideal for making breads, cookies, and crackers as it is nutritionally similar to flour, is light in color, and has a bland flavor. Teff is a cereal grown in Ethiopia and is traditionally used in the production of a fermented batter bread called *injera*. Teff is more suitable for use as a thickening agent in soups, stews, gravies, and puddings and is therefore more useful in cooking than in baking. Garfava flour is suitable for use in making bread, cakes, or cookies and contributes good nutritional value to these products.

Breads made using only starches will not require extensive fermentation times. However, a short rest is required to allow the yeast to create sufficient aeration. In some recipes, however, chemical aerating agents are used to provide the aeration, and the yeast is added mainly for its contribution to the flavor and aroma of the bread.

Gluten-free bread is produced by replacing the flour with a mixture of fine rice flour, potato starch, and tapioca flour. Xanthan gum is added to provide the product with structure and prevent crumbliness. The proportion of water has been adjusted to allow for the different water absorption and adsorption rates of the starches and gum used. In the gluten-free bread making process the 1-hour bulk fermentation time is not required; only the final proof is needed to bring the product up to the volume required. The recipe given (Table 37.1) produces a product with the flavor, aroma, and texture of bread but that does not necessarily possess the mouthfeel expected of bread. Toasting slices of the gluten-free bread improves the mouthfeel. Variations to the recipe (Table 37.1) by the addition of savory flavorings such as herbs, sundried tomatoes, and olives and by baking the product in a round cake pan not only improve the overall flavor but also provide a product with a better aesthetic appearance.

Table 37.1 Standard bread recipe with conversion into a gluten-free bread recipe

Standard bread recipe[a]		Gluten-free bread[b]	
Ingredients			
<Strong flour	100%	Rice flour	67%
		Potato starch	22%
		Tapioca flour	11%
Salt	2%	Salt	1.5%
Sugar	1%	Sugar	2%
Milk powder	1%	Milk powder	5%
Fat	2%	Xanthan gum	0.5%
Yeast (compressed)	2%	Oil	2%
Water	62–64%	Yeast (compressed)	1.5%
		Water	110%
Yield			
1 kg (2 lb) of flour will give two loaves weighing 780 g (1 lb 11 oz) after baking		1 kg (2 lb) of starch will give two loaves weighing 800 g (1 lb 12 oz) after baking	
Specifications			
Method: Mix all the ingredients together until well developed dough is formed.		Method: Combine all the ingredients together into a smooth batter.	
Dough temperature: 26 °C (79 °F)		Batter temperature: 30 °C (86 °F)	
Bulk fermentation time: 1 h Knock back: at 40 min Scale, round, mold, tin, or tray up and then final proof for 45 min. Bake at 230 °C (446 °F) for 25 min		Deposit into greased tins and final proof 60 min (allow the batter to double in volume). Bake at 210 °C (410 °F) for 40 min	

[a] One-hour bulk fermentation, as used in Australia, New Zealand, and the United Kingdom.

[b] As adapted from Hagman 2000.

Lactose intolerance

Lactose is the double sugar found in milk and is therefore found in all dairy products. Lactose intolerance is not as common as gluten intolerance and is less of a challenge to baking because milk and milk powder have a smaller role to play in baked products.

Milk can be easily replaced by using soy milk. Soy milk is suitable for all baked products that require the addition of milk, including its use as a replacement for milk in milk custard-based fillings. In order to replicate the richness of a quiche filling, which often requires the addition of a proportion of cream in addition to milk, the cream may be replaced by 80% of soy milk and 10–15% of vegetable oil. Rice milk (made by blending cooked rice and water together) and the milk from nuts like almonds and coconut are also suitable for use as substitutes for milk.

Whipped dairy cream may be replaced by vegetable-based "cream" filling. However, cheeses are more difficult to replicate with soy products. Soft or silken soybean curd can be successfully used to replace cream, ricotta, or mascarpone cheese in cheese cakes, both baked and cold, and in desserts like tiramisu. Firm soybean curd can be diced and used to replace feta cheese and can be used in filling quiches, savory pies, and pizza or calzone. There are also varieties of firm soybean curd that are flavored with various marinates. These may be sliced or diced and used as a substitute for cheese in savory muffins or quiche and in fillings for bread rolls, bagels, or wraps.

Soybean curd does not usually have a strong flavor, but some people detect a slight "beany" flavor, especially in soybean curd that is not as fresh as it should be. Careful use of flavorings from the zest and/or juice of lemons, limes, or other citrus fruits or spices in sweet products, and herbs and spices in savory products, will help mask the beany flavor. The vegetable proteins in soy also tend to respond to heat more readily than those in cheese, so care should be taken in baking off soybean curd/tofu based "cheese cakes."

Overbaking of soy-based products will lead to pronounced syneresis. Syneresis occurs when proteins in eggs or soy are overheated, causing the proteins to shrink and release moisture, which makes the custard look as if it has curdled.

A recipe for standard cheese cake with conversions for dairy-free "cheese cake" is shown in Table 37.2. If silken tofu only is used, a softer textured product (that will be more prone to syneresis) will be produced. Arrowroot is added to help stabilize the curds and to prevent syneresis in the finished product, so if silken tofu is used entirely, more arrowroot (up to 5%) can be added. Other starches like potato starch or tapioca starch may also be used. The juice and zest of other citrus fruits may be used instead of lemons. If spices are preferred as flavoring (cinnamon or nutmeg are good choices), the lemon juice and water may be replaced with other fruit juices; apple juice is more neutral, but other juices like grape or pineapple are also suitable.

Table 37.2 Standard baked cheesecake recipe with conversion into dairy-free "cheesecake"

Baked cheesecake[a]		Baked dairy-free cheese cake or tofu cheese cake[b]	
Ingredients			
Cream Cheese	100%	Silken/soft tofu	50%
		Firm tofu	50%
Castor sugar	23%	Castor sugar	20%
Eggs	26%	Vanilla essence	0.5%
Vanilla Essence	0.8%	Lemon zest	1%
Lemon zest	0.8%	Lemon juice	3.5%
		Arrowroot	2%
Yield			
1.5 kg (3 lb) of cream cheese makes a cake 20 cm (8 in) in diameter and 6 cm (2½ in) high		1 kg (2 lb) of tofu will make a cake 20 cm (8 in) in diameter and 5 cm (2 in) high	
Specifications			
Method: Combine all the above ingredients, in a cake mixer, into a smooth batter. Deposit into well greased and floured tins. Bake at 200 °C (390 °F) in a water bath for 60 min and followed by 160 °C (320 °F) for 20 min. Cool thoroughly and refrigerate overnight before detinning each cheesecake on to a prebaked sweet pastry disc.		Method: Combine all the ingredients to a smooth puree in a blender or food processor. Pour into a tin that has been prelined with a par-baked crumb base (ensure that the crumb base is made with dairy-free cake, biscuit or bread crumbs bound together with oil). Bake at 180 °C (356 °F) for 1 h in a water bath. Cool thoroughly before serving.	

[a]Based on cream cheese weight.

[b]Based on weight of tofu.

Honey or maple syrup may also replace castor sugar, but as they are liquid sweeteners, the water level will need to be lowered to allow for the extra moisture.

The overall presentation of the product is also improved by placing fruit filling onto the base of the par-baked crust before the tofu cheesecake is deposited into the base and baked. Decoratively arranging fresh or tinned fruit on the top of the baked and cooled tofu cheesecake will also produce a more impressive appearance.

Egg allergy

Egg-free baking is possible with a large range of bakery products. Most breads, pastries, and biscuits/cookies can be made egg free by replacing the moisture content that is contributed by eggs with milk or other liquids. However, cake and sponge making are heavily reliant on the functional characteristics of eggs as a mechanical aerating medium.

Commercial egg replacers may be used. They are made up of potato starch, tapioca flour, a

chemical leavener, and carbohydrate gum. Egg replacers are only useful as a binding and moistening agent.

Soy flour with a protein dispersibility index of 70% can be used to replace the egg component in the production of sugar cookies, chocolate cake, muffins, and pancakes (Gilbertson and Porter 2001). The addition of lecithin into the product improves overall volume, texture, and eating quality.

The gummy exudates from ground flaxseed are another source of egg replacer. Flaxseed is first ground up in an herb or coffee mill. The ground powder (with an equal amount of water added) is then mixed in a food processor to extract the gummy exudates. In quantity, 25 g (1 ounce) of flaxseed plus 25 ml (1 fluid ounce) of water equals one egg, and the exudates from the flaxseed are then used to replace eggs in cakes, biscuits, and custards (Stepaniak 1998). Flaxseed has a very short shelf life and is prone to rancidity. Therefore, the exudates from flaxseed have to be prepared from fresh seeds.

All of the egg content in the chocolate cake recipe (Table 37.3) can be replaced by soy flour and water. Oil replaces the butter, lowering the amount of saturated fat in the recipe. Baking soda is used in both of the recipes to produce a darker crumb color. Bleached cake flour (high-ratio flour) may be used instead of white baker's flour. The moisture content can then be increased by 10%, with increased mixing time.

Table 37.3 standard chocolate cake recipe with conversion into eggless chocolate cake

Standard chocolate cake		Eggless chocolate cake	
Ingredients			
Flour	100%	Flour	100%
Cocoa powder	20%	Cocoa powder	22%
Baking powder	6%	Baking powder	6.2%
Baking soda	2%	Baking soda	1.5%
Castor sugar	80%	Soy flour	22%
Butter	80%	Castor sugar	100%
Eggs	80%	Oil	85%
Milk	15%	Lemon juice	15%
		Water	180%
		Vanilla essence	2.5%
Yield			
500 g (1 lb 1 oz) of flour will make a cake 20 cm (8 in) in diameter and 5 cm (2 in) high		500 g (1 lb 1 oz) of flour will make a cake 20 cm (8 in) in diameter and 5 cm (2 in) high or two cake layers 20 cm (8 in) in diameter and 2½ cm (1 in) high	
Specifications			
Method: Sugar batter method. Cream the butter and sugar until light in texture and color. Gradually beat in the warmed eggs. Fold in the dry ingredients (flour, cocoa powder, baking powder, and baking soda), which have been sifted together. Combine together until just smooth and then mix in the milk. Deposit into greased or papered tins. Bake at 180 °C (356 °F) for 25 min.		Method: All-in method. Place sugar, oil, lemon juice, water, and vanilla essence into a mixing bowl. Sift the dry ingredients (flour, cocoa, baking powder, baking soda and soy flour) together and add to the wet ingredients. Combine on slow speed in a cake mixer. Mix on medium speed for 2 min. Deposit into greased tins. Bake at 180 °C (356 °F) for 25 min.	

Since no eggs are used in the eggless chocolate cake, the product is delicate to handle. Although not a problem when the cake is sold with just a simple icing sugar dusting on the top, the addition of 0.2% xanthan gum will help to provide greater strength if the cake has to be iced and packed for sale.

Bakery products that contribute to a healthier lifestyle

The incidence of obesity has increased markedly in many developed countries. In the United States, an estimated 34.2 % of adults aged over 20 years are overweight. Of these, 33.8% are obese and 5.7% are extremely obese (Ogden and Carroll 2010). In England, 22% of adults aged 16 and over are classified as obese (NHS 2011). In Australia, statistics indicate that 3 in 5 adults (61%) and 1 in 4 children (25%) aged 5–17 are overweight or obese (Australian Institute of Health and Welfare 2010). Based on a 2006/2007 survey, 1 in 4 (26.5%) of adults in New Zealand were obese (Ministry of Health, New Zealand 2011).

Traditionally, consumers who are trying to lose weight have perceived bakery products as products to avoid. Therefore, there has been an increase in baked products that are marketed as low fat, low sugar, and/or high fiber.

However, there is a large range of bakery products that are already low fat, low sugar, and/or high fiber. These include wholemeal or wholegrain breads, most artisan/hearth-type breads (brown, white, or rye), sponge cakes (chiffon and devil's food cakes), and biscuits like biscotti and macaroons.

Fat replacers and alternative sweeteners can be used in the development of low-fat, low-sugar products. However, in this section, conventional ingredients will be used to reduce fat and sugar levels and increase fiber levels in bakery products (Table 37.4).

Table 37.4 Conventional blueberry muffin with conversion into low-fat healthy muffin

Conventional blueberry muffin		Low-fat healthy muffin	
Ingredients			
White baker's flour	100%	Wholemeal flour	100%
Baking powder	6%	Baking powder	3.2%
White castor sugar	50%	Soft brown sugar	35%
Eggs	25%	Eggs	20%
Oil	33%	Oil	20%
Milk	50%	Milk	72%
Vanilla essence	0.4%	Vanilla essence	0.4%
Blueberries	40%	Blueberries	40%
Yield			
250 g (8½ oz) flour will make 12 standard sized muffins		250 g (8½ oz) flour will make 12 standard sized muffins	
Specifications			
Method: Place the eggs, oil, milk and vanilla essence in a mixing bowl. Add the sugar and combine for 2 min. Add the sifted dry ingredients (flour and baking powder) and mix until just combined. Gently fold in the blueberries. Deposit into muffin papered lined muffin tins. Bake at 210 °C (410 °F) for 20 min.		Method: As for conventional muffins.	

Wholemeal flour is used in the healthier muffin (Table 37.4) to increase the fiber content of the product. Lower levels of eggs, oil, and sugar are used, with an increase in milk content to replace the moistening and softening functions of these ingredients. To further reduce the fat content in the muffins, use reduced fat milk, skimmed milk, or soy milk instead of full fat milk. In many "gourmet" muffin varieties, the additional ingredients (dark or white chocolate pieces, dried fruit in sweet muffins, and cheese or ham/bacon in savory muffins) tend to add high amounts of fat and/or sugar to the product. Varieties that make use of more healthy combinations of additional ingredients will appeal to customers seeking out healthier alternatives. Some healthier examples include cranberries and carob instead of apricots and chocolate chips, and broccoli and marinated tofu instead of bacon and cheese.

Bakery products for specialized diet requirements (diabetes)

Diabetes occurs when there is "too much sugar in the blood" and is caused by the body's inability to produce insulin or the body becoming insensitive to insulin. Insulin is produced by the pancreas, and its function is to help the body cells absorb glucose from the blood and to regulate the amount of glucose that is available in a person's bloodstream at any one time. There are two types of diabetes: insulin-dependent diabetes (type 1) and non-insulin-dependent diabetes (type 2). People with type 1 diabetes require insulin injections and a healthy diet to stay well. Eighty-five percent of people with diabetes have type 2 diabetes, which can be controlled by a healthy diet and exercise, as losing weight is the most important part of type 2 diabetes treatment (Roberts and others 1995).

Baking for people with diabetes requires that the products be kept low in fat, and some changes are made to sugar use in baked products. The functions of sugar in baking include the following:

- *Acting as a sweetening agent*. Synthetic sweeteners are used as alternative sweeteners in baked products that do not contain sugar. Products that are suited to the use of alternative sweeteners include cake and pie fillings, cake and sponge products, and a range of dessert products (mousses, ice creams). Different countries will allow the use of a different range of alternative sweeteners, so it is important to check on the legality of the use of various alternative sweeteners specifically in baked products. Alternative sweeteners that are permitted in food under the US Food and Drugs Act (FDA) are acesulfame K, aspartame, and sucralose (Nelson 2000). Under the Australian and New Zealand Food Standards (2001), acesulphane K (acesulfame K) and alitame are allowed for use in flour products and in biscuits, cakes, and pastries. Use of sugar alcohols like sorbitol, maltitol, hydrogenated starch hydrolysates, xylitol, lactilol, mannitol, and isomalt is generally allowed in most countries (Nelson 2000). Some alternative sweeteners (aspartame is the main example) cannot withstand baking temperatures and will not then contribute to sweetness in the final product. An exception would be sucralose, which is derived from cane sugar. Sucralose is more sugar-like in taste and stability and is suitable for use in baked products, baking mixes, and various frostings, fillings, and icings (Chapello 1998).

- *Providing yeast food in bread products*. The sugar that is used in bread making to help provide yeast with a source of food may be omitted in yeast products or replaced with a diastatic malt product.

- *Acting as a softening/tenderizing ingredient*. Sugar helps make cakes and breads softer and more tender to eat. An increase in moisture via the use of apple puree, crushed pineapple, or canned or fresh fruit pulp (apples, peaches, apricots etc.) will help tenderize cakes, muffins, or fruit loaves. Replacing any liquid in the product with fruit juice will also help.

- *Contributing crispiness in biscuits/cookies*. Small amounts of sugar will still be needed to assist in keeping cookies crisp. The sugar alcohols sorbitol, maltinol, and xylitol are hygroscopic and are not recommended in products that require a degree of crispiness (Nelson 2000).

- *Aiding in mechanical aeration when sugar is beaten with shortening/butter or eggs.* Conventional cake making methods will need to be modified slightly to offset the small amount of aeration lost because sugar is not present to help draw air into the batter during mechanical aeration.

- *Helping to prevent mold (especially in cake products).* The high levels of sugar in high-ratio cakes help to prevent mold growth on these products. A lower level of sugar will therefore need to be offset with a lower pH. This may be achieved by using low pH products like lemon juice or buttermilk in the recipe in place of milk or water and by using small amounts of cream of tartar or similar products.

- *Providing crust color in products.* Most alternative sweeteners will not undergo Maillard browning, and none will caramelize. The addition of milk powder or whey powder will help enhance crust color in all baked products. Often, only small amounts of the alternative sweetener are used, so flavors and colors may need to be added to contribute to the desired crust flavors and browning effects (Nelson 2000).

A conventional banana bread recipe with conversions for diabetic banana bread is presented in Table 37.5. As with all products that utilize the acidity in ripe bananas to react with the alkali in the baking soda to provide for chemical aeration, one must ensure that the bananas are very ripe. The sweetness in the ripened bananas should be sufficient to provide enough sweetness to the diabetic banana bread recipe.

Table 37.5 Conventional banana bread with conversion into diabetic banana bread

Banana bread (conventional)		Diabetic banana bread	
Ingredients			
Baker's flour	100%	Baker's flour	45%
		Whole-meal flour	45%
		Rolled oats	10%
Baking soda	4%	Baking soda	2.2%
Bananas	100%	Baking powder	2.2%
Castor sugar	100%	Bananas	100%
Eggs	50%	Lemon juice	30%
Milk	27.7%	Corn oil	20%
Corn oil	27.7%		
Yield			
450 g (1 lb) of flour will make one large loaf in a tin (28 cm [11 in] × 11 cm [4½ in] × 80 cm [3 in] or two loaves in tins (21 cm [8 in] × 10 cm [4 in] × 6 cm [2½ in])		450 g (1 lb) of flour will make one large loaf in a tin (28 cm [11 in] × 11 cm [4½ in] × 80 cm [3 in]) or two loaves in tins (21 cm [8 in] × 10 cm [4 in] × 6 cm [2½ in])	
Specifications			
Method: Combine bananas and sugar in a cake mixer until smooth. Gradually add the eggs, then the milk and oil. Sift the flour and baking soda and blend into the batter. Deposit into paper-lined tins and bake at 200 °C (392 °F) for 1½ hrs.		Method: Combine bananas, lemon juice, and oil to a smooth paste. Blend in the sifted flour, wholemeal flour, baking powder, and baking soda. Deposit into paper-lined tins. Bake at 180 °C (356 °F) for 40 min.	

If more sweetness is required, a small amount of alternative sweetener may be added to the product, or 10% honey, maple syrup, or golden syrup may be used.

The sugar level from the bananas is offset by the higher fiber content contributed by the use of wholemeal flour and rolled oats in the diabetic banana bread.

Bakery products for special religious diet requirements

Many religions encourage their adherents to follow prescribed rules with regard to the foods that are allowed to be eaten. Strict followers of Buddhism and Seventh Day Adventists are often also vegetarians, and many are vegans. Hindus will not eat any food that contains traces of meat from cows. In this section, baking products for orthodox Jews (kosher baking) and strict adherents to the Muslim faith (halal baking) are discussed, as these two religions have a large number of followers, and their religious prescriptions for food are often seen to be more complex by non-Jews/non-Muslims.

Kosher baking

Kosher means "the selection and preparation of foods have been carried out in accordance with traditional Jewish ritual and dietary laws" (Kaye and Rance 1986). Foods that are acceptable include "meat from animals with cloven hooves that chew cud," but "camel, horse, hare, pig, and donkey are prohibited" (Nash 1988). The hindquarters of the animals that are allowed to be eaten are also prohibited. All birds are allowed except for those that are carnivorous. All the allowed animals must be ritually slaughtered and prepared. Fish with removable scales and fins are allowed, but shellfish is prohibited. Gelatin is also not allowed.

Meat *(pareve)* and dairy products must be kept apart at all times, so dishes, utensils, and washing-up areas must be allocated separately for meat and dairy products.

Milk or recipes containing milk or other dairy products may be eaten before meat at a meal, although the mouth should be "cleaned" by eating bread, for example, in between (Kaye and Rance 1986). However, dessert containing milk or milk products cannot be eaten after meat until at least a 3 h interval has elapsed. The previous section in this chapter on lactose intolerance can be used to provide information on substitutes for milk in baked products and desserts.

Halal – baking for Muslims

One of the *Shri'ah* (divine laws) in Islam revolves around strict food laws. The holy book of Islam, the Qur'an, forbids "the consumption of pork, blood, carrion, or food which has been sacrificed to idols" (Van der Krogt 1990). In practice, Muslims will not eat products that have any traces of pig, reptiles, carnivorous animals, or animals that are not slaughtered using the correct procedure. Alcohol is also forbidden. Foods that are suitable for consumption by Muslims are termed *halal*. Halal is defined as "released from prohibition" and implies "that which is lawful" (Bowker 1998).

A recipe for traditional fruit mousse with conversions for kosher/halal fruit mousse is presented in Table 37.6. The setting agent agar is used to replace gelatin. Agar is available as a powder or as dried transparent strips. It must be brought to the boil with water before it will set. Agar sets at room temperature and tends to set firmer than gelatin. The cream and eggs in the traditional mousse are replaced with soft (silken) tofu. The modified mousse is a versatile recipe that lends itself to many possible variations. Any soft fruit in season is suitable for use. Agar is also stable against proteolytic enzymes, so traditional fruits that cannot be used raw in gelatin-set desserts (kiwifruit, pineapples) may be used with agar.

However, watch that the acidity in the fruit puree used in making the mousse is not too high (raspberries and blackberries, especially), as the tofu will tend to separate under high acidity conditions.

Table 37.6 Traditional fruit mousse with conversion into kosher/Muslim fruit mousse

Traditional fruit mousse[a]		**Kosher/Muslim fruit mousse[b]**	
Ingredients			
Fruit puree (berry fruits or stone fruits)	70%	Whole fruits (berry fruits or stone fruits)	130%
Sugar	20%	Apple juice	45%
Gelatin	2.4%	Agar powder	1.6%
Water	10%	Silken tofu (soft soybean curd)	100%
Fresh cream (whipped)	100%	Honey	35%
Egg whites	24%	Vanilla essence	2%
Sugar	20%		
Water	8%		
Yield			
250 ml (8 fl oz) of cream will produce sufficient mousse to fill one gateau/torte 20 cm (8 in) diameter to a thickness of 3 cm (1½ in)		300 g (10 oz) of tofu will produce sufficient mousse to fill one gateau/torte 20 cm (8 in) diameter to a thickness of 3 cm (1½ in)	
Specifications			
Method: Prepare an Italian (boiled) meringue by boiling the 20% of sugar with the 8% of water to the soft ball stage (118 °C/240 °F) and pouring the syrup into egg whites whisked to a soft peak. Soak the gelatin in the 10% water, and when it has swelled up well, dissolve the soaked gelatin in fruit puree that has been brought to the boil but taken off the heat. Combine the Italian meringue into the fruit puree and then fold in the lightly whipped fresh cream. Use the mousse as required.		Method: Combine the agar and apple juice together and bring to the boil. Place the silken tofu, honey, fruit, and vanilla essence into a blender/food processor and combine well. Add the agar and apple juice and mix in thoroughly. Use the mousse as required.	

[a]May be used as a filling for gateaux or torten or served as individual desserts. Recipe based on percentage of fresh cream.

[b]May be used as a filling for gateaux or torten or served as individual desserts. Recipe based on percentage of tofu.

Bakery products suitable for lifestyle choices

In this section, bakery products that fit into the lifestyle choices of certain sectors of the community and can be easily adapted are profiled. Sports nutrition and baking for vegetarians and vegans are considered in this section.

Sports nutrition

Sports nutrition is a specialized area concerned with enhancing the sports performance of athletes through the proper selection of foods. Diet is an especially important aspect of being a competitive sports person. Specific diets are created by nutritionists for specific sports (Burke 1995). Without the correct fuel in their bodies, sports people might as well not start their events.

Sports people tend to view food as fuel for their bodies as they indulge in the sporting endeavor of their choice. When you look at food solely from the energy provision viewpoint, the terms *high glycemic index* and *low glycemic index* will be encountered.

In summary:

- High glycemic index foods are required at the end of a bout of energetic exercise to replace sugars used up by the muscles during the activity. High glycemic index foods are absorbed into the bloodstream quickly and are made up of foods like white bread, rice, potatoes, and sugars (like honey and glucose).

- Low glycemic index foods can be used by the body to store up energy for peak and enduring performance by athletes. Low glycemic index foods are high in starches, take more time to be absorbed by the digestive system, and are suitable for storage as glycogen in the muscles (foods with a low glycemic index include pasta, porridge, and wholemeal and wholegrain breads).

In theory, this means that sports people tend to have to "carboload" on low glycemic index foods while they are in training and leading up to their sports event (Colgan 1993). High glycemic index foods may be taken during the event to help provide extra short bursts of energy and after the event to replenish depleted energy supplies.

- **High Carbo Calzone**. This calzone may be made into small individual pasty-sized items or into a 25–30 cm (10–12 inch) round "mega" calzone.

- Use 100 g (3½ ounces) of pizza or bread dough for the individual calzones and 500 g (1 pound) dough for the mega calzone. Pin out the dough into a circle, place about 100–150 g (3½ to 5 ounces) of filling for the individual calzones and 500–600 g (1 pound to 20 ounces) of filling for the mega calzone. Shape the calzone like a pasty (crimp the edges). The large calzone may be made by using two circles of dough to enclose the filling and then sealing the dough together by crimping up the edges.

- The filling is made by cooking a pasta such as macaroni, small spirals, or seashells until it is just soft *(al dente)*. Toss the pasta in pesto (basil, pine nuts, and parmesan cheese), tapenade (olives), or a tomato-based pasta sauce. Season well with herbs, sea salt, and pepper. Add small amounts of low-fat protein like ham, pastrami, smoked chicken, or seafood (such as tinned tuna or salmon). To add color, texture, and flavor, use a small amount of vegetables such as red, green, or yellow peppers, or red or green courgettes. Add some cheese, preferably mozzarella, but cheddar is acceptable. Use lots of pasta as this is an ideal low glycemic index food, and it makes the product more cost effective to produce. It is important to keep the filling ingredients low in fat as athletes prefer a high protein, high carbohydrate, but low-fat diet.

- Egg wash the calzone well before proofing it and then baking it in a 210 °C (410 °F) oven with solid bottom heat. Refrigerate the product once it is baked. Calzones also freeze well and are best reheated from the frozen state by placing them, directly from the freezer, into a preheated oven set at 200 °C (392 °F).

- The filling used in the calzone can be varied by changing the type or shape of pasta, the pasta sauce, or the additions. Strive for low-fat, protein-based products, and use vegetables that are high in carotenoids and other antioxidants.

Vegetarianism and veganism

There are steady numbers of people professing to be vegetarians or vegans. In Canada, vegetarians or vegans are estimated to make up between 4 and 10% of the population. In the United States, the proportion is about 3% for vegetarians and 1% for vegans, and in the United Kingdom, an estimated 2% of the population are vegetarians (Harris 2009).

Vegetarians will not eat food of animal origin. There are various degrees of vegetarianism. Lacto-vegetarians will eat dairy products and lacto-ovo vegetarians will eat dairy products and eggs. Vegans will not eat any product that has had any contact with animals or materials of animal origin. Very strict vegans will not eat foods that contain processed cane sugar (as cane sugar refining involves filtering the sugar syrup through carbonized bone meal), vegetable oils (which are also refined through products that have an animal origin), or honey. Beet sugar (which is refined using a different method than that used for cane sugar) and cold-pressed vegetable oils are suitable for use in vegan products. Other ingredients of animal origin that are anathema to vegans include emulsifiers such as calcium stearate, mono-, di-, and triglycerides, lecithins, sodium stearoyl, polysorbates and glycerols, flavor enhancers

containing monosodium glutamate, gelatin and isinglass, and enzymes derived from animals (including pepsin and rennet). Vitamin supplements (A and D in particular) that may be derived from egg yolks or fish oils are also to be avoided (Stepaniak 1998).

Many vegetarians will depend on bakery foods for their food choices, as many bakery products can be made without the use of ingredients that have animal origins. A wide range of bakery products can be made using vegetable oils (or shortenings based on hydrogenated vegetable oil) instead of animal-based fats, and the food intolerances section in this chapter provides alternatives to dairy products and eggs in baking. So, baking for vegetarians is much more straightforward than baking for vegans. Vegan baking requires bakers to be philosophically and ethically committed to the challenge of baking without cane sugar, dairy products, eggs, or refined oils.

A recipe for carrot cake with conversions for vegan carrot cake is shown in Table 37.7. Rice milk, coconut milk, or other nut milks may be used in place of soy milk. This recipe may also be varied by substituting other firm vegetables for the carrots. Courgettes, beetroot, pumpkins, parsnips, and taro may all be used. Vary the spices and nuts to suit each vegetable that is used. As examples, parsnip may be teamed with nutmeg and Brazil nuts, and pumpkins with ginger and hazelnuts.

Table 37.7 Carrot cake (conventional) with conversion to vegan carrot cake

Carrot cake		Vegan carrot cake	
Ingredients			
Baker's flour	100%	White baker's flour	50%
		Wholemeal flour	50%
		Cinnamon	0.8%
		Cloves	0.2%
Baking powder	2.2%	Baking powder	3%
Salt	1.3%	Salt	0.8%
Baking soda	1.3%	Cold pressed virgin olive oil	44.4%
Corn oil	50%	Beet sugar	47.2%
Eggs	80%	Soy milk	52.7%
		Lemon juice	4.2%
		Vanilla essence	1.4%
Castor sugar	150%	Grated carrots	45.8%
Grated carrots	135%	Walnut halves	16.6%
Walnuts (chopped)	80%		
Yield			
450 g (1 lb) of flour will make one 20 cm (8 in) diameter cake that is 6 cm (2 ½ in) high		450 g (1 lb) of flour will make one 20 cm (8 in) diameter cake that is 6 cm (2 ½ in) high	
Specifications			
Method: Combine the corn oil, eggs, and sugar together and mix until smooth. Stir in the sifted dry ingredients (flour, baking powder, salt, and baking soda) and then fold in the carrots and walnuts. Deposit into greased or paper-lined tins. Bake at 180 °C (356 °F) for 40 min.		Method: Combine the olive oil, soy milk, lemon juice, and vanilla essence together. Add the beet sugar and mix until the sugar is dissolved. Add the sifted dry ingredients (flour, whole-meal fl our, baking powder, cinnamon, cloves, and salt. Add the carrots and walnuts. Deposit into greased or paper-lined tins. Bake at 180 °C (356 °F) for 40 min.	

Bakery products suitable for various stages of human development

In this last section, the stages of human development are taken into account when bakery products are devised. The special nutritional requirements for younger children (between ages of 4 and 8 years); women, in particular adolescent women, pregnant women, and menopausal women; and seniors (consumers over the age of 60) are discussed.

Baking for young children

Younger children who are provided with a wide choice of healthy foods will tend to continue a healthy eating lifestyle. Many bakery foods are made to be bright and colorful for younger children. This also brings with it a responsibility for bakers to keep the level of colorings used low and to use colorings that are proven to be safe.

Greaves (2002) provides details of the food colors that are allowed for use in the United States and advocates the use of natural colorants derived from beetroot, grape juice, and saffron. He also warns of the need to select the correct coloring to be used, as some natural colors are prone to a lack of stability, giving rise to shade changes in batters of different pH, fading of the color after baking, and phase separation of the coloring itself from the medium it is mixed into.

As in adults, obesity in children is the "major nutrition-related disorder" (Tuttle and Truswell 2002). Therefore, lowering the fat and sugar content and raising the fiber content of baked products will help produce a healthier product. The chocolate chip cookie recipe shown in Table 37.8 is an example of how this can be achieved.

Table 37.8 Chocolate chip cookies with conversion to healthier version

Standard bread recipea[a]		Gluten-free breadb[b]	
Ingredients			
Baker's flour	100%	White baker's flour	30%
		Wholemeal flour	70%
Baking soda	1.5%	Baking soda	2%
Salt	1.5%	Corn oil or canola oil	60%
Butter	60%	Maple syrup or golden syrup	35%
Brown sugar	42%	Water	25%
Granulated sugar	42%	Vanilla essence	2%
Eggs	24%	Chocolate or carob chips	60%
Hot water	7.1%		
Vanilla essence	2.3%		
Chocolate chips	60%		
Yield			
450 g (1 lb) of flour will make 32 cookies of 5 cm (2 in) diameter		450 g (1 lb) of flour will make 32 cookies of 5 cm (2 in) diameter	
Specifications			
Method: Cream butter and brown and granulated sugars together. Gradually add the eggs, hot water, and vanilla essence and cream until light. Add the chocolate chips and fold in the sifted flour, baking soda, and salt. Shape into a cylinder approximately 5 cm (2 in) in diameter. Wrap in plastic wrap and chill. Slice into 0.5 cm (1/4 in) slices and place on a lightly greased tray. Bake at 180 °C (356 °F) for 15 min.		Method: Stir the corn oil, syrup, vanilla essence, and water together. Add to the sifted dry ingredients (flour, whole-meal flour, and baking soda) and mix until the dough just combines. Add the chocolate chips and bring the dough together until well combined but do not over mix. Drop the mixture onto lightly greased trays and flatten into a round shape. Bake at 180 °C (356 °F) for 15 min.	

In the healthier version, the chocolate chips provide the main flavor in the product. Oil and syrup are used to provide shortening and softening to the biscuit with the use of wholemeal flour for higher fiber and added crunchiness. It is important to use a high grade, almost flavorless oil, as the flavor of the oil will carry through into the cookies. Also, ensure that the cookies are shaped to the correct thickness and sufficiently baked to achieve a crisp product.

Baking for women

Adolescence is the period of life between the onset of puberty and full maturity, and in young women there are extra nutritive requirements, including those for higher levels of calcium, iron, and folate, for coping with increased growth and the onset of menarche. Lifestyle changes brought about by growing independence and intense concern with appearance and weight and a need for peer acceptance also define eating behaviors (Story and Alton 1996).

> **Multigrain rolls**
>
> - *Formulation.* Flour (100%), flaxseed (10%), milk powder (2%), sugar (1%), yeast (2%), soy grits (10%), salt (1.5%), soy flour (1%), soybean oil (2%), water (63–65%).
> - *Yield.* 1 kg (2 pounds) of flour will give 24 bread rolls scaled at 60 g (2 ounces) each.
> - *Method.* Soak the flaxseeds and 10% of the water for 2 h. Combine all ingredients and mix to produce a well-developed dough.
> - *Dough temperature.* 26 °C (78 °F).
> - *Fermentation and proofing.* Bulk fermentation time – 1 h. Knock back – 40 min. Scale into rolls [60–80 g (2–3 ounces) each], round, mold, and then final proof for 45 min.
> - *Baking.* Bake at 230 °C (446 °F) for 15 min.
> - *Consumption.* Fill the rolls with lean meat, sprouts (alfalfa, snow peas, or soy), a relish that enhances the meat being used, and sliced tomatoes, grated cheese, and lettuce.

The most nutritionally demanding period in a woman's life is during her pregnancy. Sufficient nutrition must be provided not only to the mother but also for the developing fetus. A higher than required amount of calcium and iron is required not only during pregnancy but after the birth of the baby (Lovelady 1996).

Recent research has highlighted the special dietary needs of postmenopausal women. A diet rich in phytoestrogens, which is found in soy products and flaxseeds, helps alleviate the symptoms of menopause and plays a role in the prevention of breast cancer and the development of melanomas. (It may also help prevent prostate cancer in men) (Payne 2000). Calcium, along with adequate vitamin D and load-bearing exercise are also required to prevent the onset of osteoporosis in postmenopausal women (Chernoff 1996).

> **Salmon and kumara (sweet potato) wholemeal quiche**
>
> - Make a wholemeal short pastry and line a flan ring or quiche tin with it. Make large, deep dish quiches and some individual ones as well.
> - Fill the quiche with egg custard, tinned salmon flakes, roasted *kumara* cubes, cubes of firm tofu, and a small amount of shredded silver beet (Swiss chard) and top with herbs and dollops of low-fat cream cheese.
> - Bake at 190 °C (374 °F) for 30–45 min (depending on the size of the quiche).

Baking for seniors

Aging populations result from a decline in overall fertility and increasing life expectancies in different parts of the world (Lutz and others 2008). The world's population of people aged 65

and older is now growing by an unprecedented 800,000 people a month (Kinsella and Velkoff, 2001). Worldwide, the number of people aged 60 years and over will exceed one billion in the next decade (Popper and Kroll, 2003).

Seniors have special and unique dietary requirements. These include a higher need for calcium (especially in estrogen-deprived postmenopausal women) (Chernoff 1996), greater need for vitamins D, B_6, and B_{12}, but a lower need for vitamin A. Some seniors are also at risk of being deficient especially in zinc, magnesium, and folate. The groups most likely to be at risk with poor dietary intake in old age include low socioeconomic status individuals and older men living alone. Other negative influences include physical disability, difficulties with access to shopping, depression, and chewing problems associated with the loss of teeth and poorly fitted dentures (Horwath 2002).

Bakery products could play a role in providing healthy food for seniors as most baked products are produced ready to eat, without the need for further preparation. To meet the specific dietary demands of seniors, products that are high in fiber, high in calcium and vitamin B, and are easy to chew are required.

This recipe builds on the concepts introduced above. It is high in fiber, high in calcium, high in protein and minerals, and low in fat. *Kumara* is the Maori name for a sweet potato that is grown in New Zealand. It is high in carotenoids and fiber (Lister 2003). Roasted *kumara* will have a caramelized surface, and this provides additional flavor to the product it is used in. Silver beet or Swiss chard is also high in carotenoids, iron, and fiber (Lister 2003). Spinach provides similar benefits, but silver beet better resists sustained heating and keeps its green color better within a quiche product.

Conclusion

Consumer expectations for the variety and selection of foods available for purchase have risen as per capita income has increased in both developed and developing countries. Customers are prepared to pay more for organic foods and foods that not only provide nutrition but also contribute to improved well-being. Products that are high in fiber and low in fat and sugar, and also contribute to specific nutritional requirements need not be boring or a chore to eat. Healthy baked products should not only provide health benefits but also taste good and eat well.

Baking products that provide for the good health of customers is an easily attainable goal for bakers.

This chapter provides ideas and guidelines that will assist bakers in producing a range of products that will be suitable for specialized dietary market segments.

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Part 7
Examples of World Bakery Products

38

Specialities from All Over the World

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Introduction

The list of speciality bakery products, especially bread, in the world is endless and it would be impossible to describe all of them. Suffice to say that if there are five bakers in a town, there will be five different kinds of bread. This is because the secret of bread making does not lie in the recipe but in the way the product is actually made. The discussion here is limited to a number of products (and their production methods) that are distinct and well-known throughout the world, with some emphasis on Belgium. For ease of reference, the countries are listed alphabetically. However, when studying this chapter, note the following premises:

- The information is limited to the description and basic baking procedures of the specialty bread products and is not designed to explain the chemistry, physics, biology, food science and food technology, and other scientific and technical details.

- The presentation assumes that the readers have some basic experience in baking and are familiar with such terms as degassing, proofing, grounding, scaling, and so on.

It is generally accepted that in countries where artisan bakers still prevail domestically and commercially, the quality of the bread will be noticeably higher than that in countries where industrial bakers monopolize the market. This is not meant to be negative towards the industrial bread makers but the business-driving forces are unique and different for each group of bakers. The artisan bakers consider themselves as craftsmen who offer choice and quality. The industrial bakers aim at efficiency and cost effectiveness. From this perspective, travelling through Europe can be a most rewarding experience. In countries, where the artisan baker is popular and preferred – for example, Belgium, France, Italy, and Switzerland – you will find a vast choice of quality delicacies (sometimes at unreasonably high prices), while in countries such as the Netherlands and the United Kingdom, you will find products with mediocre quality at relatively low prices. The same holds true for the United States.

Bakeries vary widely in terms of scale and product range. Typically they cover three main categories of products: bread and rolls; pastries such as pies and Danish; and speciality products such as cake, donuts, and so on. The flow diagram (Figure 38.1) of production of most bakery products is essentially the same. The process for pastries, cakes, and other speciality products varies slightly. The diagram gives a brief overview of inputs in the process, the processing steps, and the major waste streams. For whatever product in whichever country is discussed, the flow diagram holds true.
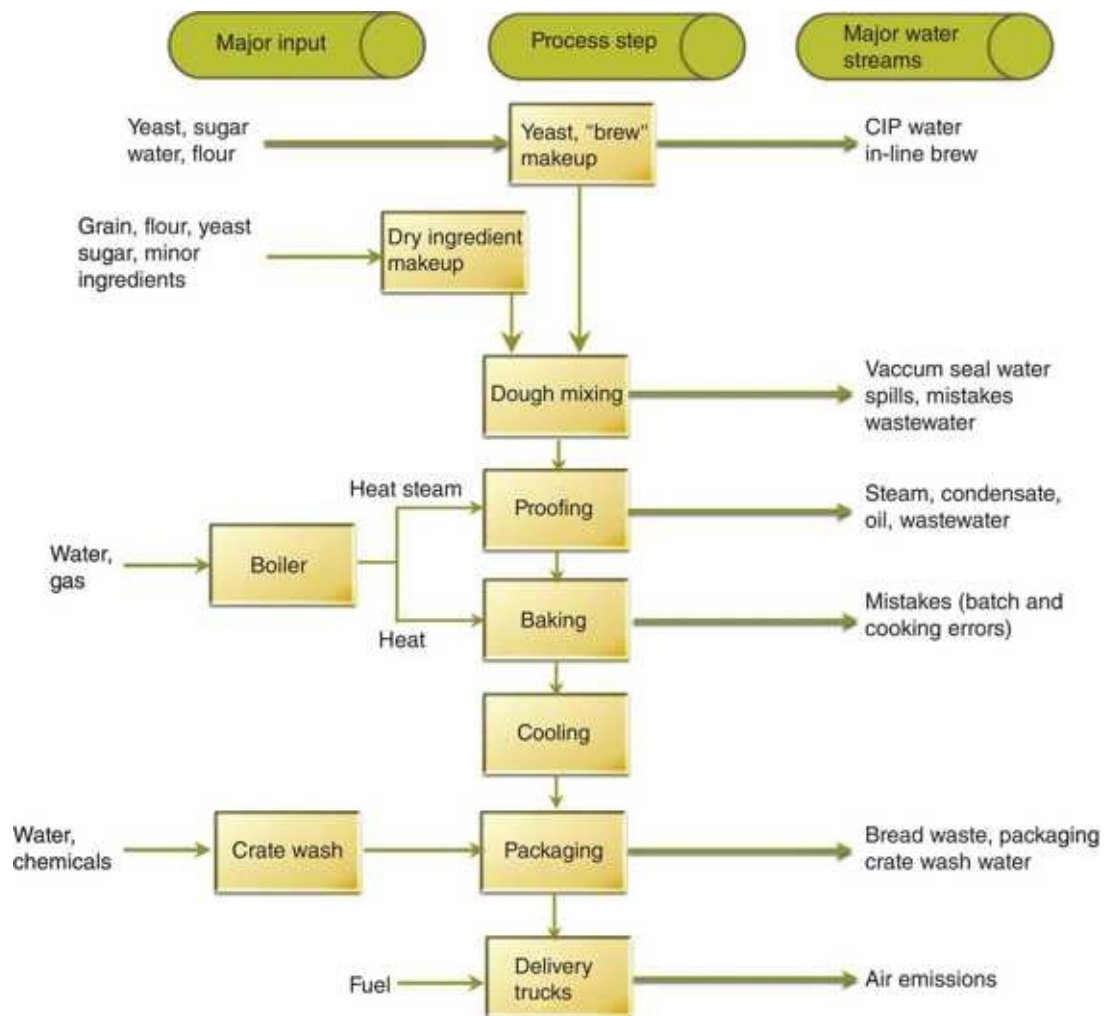
Figure 38.1 Flow chart of the production process of bakery products.

Armenia

At Easter, the Armenian baker will make *choereg*. To make it he will use the following recipe: flour (100%), water (40%), eggs (25%), butter (15%), sugar (7.5%), yeast (5%), salt (2.5%), *mahleb* (2.5%), and sesame seeds (1.5%).

Mahleb is made from the stones of dark sour cherries. The stones are ground and the resulting flour has a typical pleasant flavor. In the Middle East this product is fairly common and is available in any shop that sells herbs and spices. There is also a typical Greek product which is called *tsoureki* in which mahleb is used. Briefly, the production method is as follows.

Use lukewarm water and add the yeast and one coffee spoon of sugar. Stir until dissolved. Melt the butter without burning it. Then let it cool until it is still just liquid. Add the butter to the flour as well as the yeast suspension, the rest of the sugar, the salt, the mahleb and the eggs. Knead to develop an elastic dough, adding more water or flour if needed.

Allow the dough to rise for 3 h and mix again to obtain a degassed homogeneous product. Divide dough into equal portions of about 550 g each, shape them into strings, and plait the strings. Put the dough on a baking tray and leave to prove for 90 min. Brush with egg yolk and sprinkle sesame seeds on top. Bake the bread in a moderate oven at 170–180 °C for about 40 min until golden brown.

Belgium

In Belgium, there are a large number of real delicacies such as *boterpistolets* from Antwerp (bread rolls with butter), *roggeverdomme* (sweet rye bread with raisins), and *boterkoeken*, which are also sometimes called "expo's" by the Belgian baker. They were invented by a Belgian baker for the World Exposition of 1958. They are made from Danish pastry and have a particular shape. But one of the nicest products you can find in Belgium is *suikerbrood* (sugar loaf).

To make it one can use the following recipe: flour (100%), water or milk (60%), *parelsuiker no. 4* (50%), butter (10%), yeast (6%) and salt (2%). Parelsuiker is a pearl-shaped form of sugar, and the number 4 indicates the size (5.6–8 mm in diameter, about the size of a hailstone). This kind of sugar is a real Belgian speciality as well: it is just hard enough to melt in the dough during baking so one gets the effect of soft moist sugar patches in the crumb. These particular characteristics of the sugar make the bread exceptional. The same type of sugar is also used in the typical waffles made in the region of Liège (*gaufres liégeois*). Due to the large amount of sugar in the dough, a lot of yeast is required and the bread also has to be baked at a low temperature, or it will color (brown) quickly and may become too dark.

A well-developed dough needs to be made at about 24 °C to obtain a good sugar loaf. Let it rest for about 20 min and add the sugar, gently folding the sugar into the dough. Divide immediately into portions about 425 g each in order to make 350 g loaves. Scaling has to be done manually because the sugar, which is hard before baking, will break the safety pins in automatic dividers.

After the dough has been scaled and rounded, it is placed on aluminium trays. Normally the bread will be oval-shaped to make a flatter product, which requires less baking time than a round bread of the same weight. After proofing (40–45 min) the dough is baked in a moderate oven for about 25 min. In the northern province of the Netherlands, Friesland, a similar product is made, but it usually it contains some extra ingredients such as cinnamon and a dash of lemon peel.

For gaufres liégeois, which are made from the same recipe, the dough is divided into pieces of 55 g each and after proofing and baked using a waffle iron. "Belgian waffles" are quite well known in the United States, although most Americans are unaware of the many types of waffles in Belgium, all of which are real delicacies.

Another product which can only be found in Belgium is *pain à la Grecque* (literally means "bread made the Greek way"), but it has nothing to do with Greece. This product is mentioned here because it is one of those that seems to have disappeared from the Belgium bakery. It is painstaking to make, but once baked it is a fantastic product.

Pain à la Grecque is made from wheat flour (100%), milk (60%), yeast (10%), brown sugar (7.5%), eggs (5%), salt (1.5%), and cinnamon (0.7%). Half of the flour is mixed with all the milk, the eggs, and the yeast. The mixture is allowed to ferment for about 1 h in a cool environment, but not in the refrigerator. Then, the remaining ingredients are added and mixed until an elastic smooth dough results. The dough is allowed to rest for about 15 min and then degassed, divided into pieces of about 100 g and shaped into rectangles about 6–7 cm wide and 12–15 cm long. The pieces are flattened and sprinkled with coarse sugar. Put the

dough pieces on a well-buttered baking tray and allow to ferment for about 45 min. Degas the dough pieces again and give another proof of about 30 min. Bake for about 20 min at 180 °C. After baking, turn the baked product around and remove the rims. The product should be chewy and not dry.

Finally there is a product called *mastellen*. It is one of the few products in Belgium that contains cinnamon. In contrast to the Dutch consumer, Belgians are not too fond of cinnamon. Mastellen is a typical product of the Waasland region, which is located somewhere between Ghent and Antwerp.

To 1 kg of flour, add half a litre of milk, 75 g of yeast, 5 g of cinnamon, 300 g of butter, 20 g of salt, and 50 g of sugar. Add the butter, sugar, and cinnamon at the end of mixing when the dough is nearly fully developed. Leave the dough 30 min to prove and then divide in to 55 g pieces. Shape the pieces into round balls and leave to rest for about 15 min. Make rings out of the dough pieces similar to bagels or doughnuts. This is done in one of two ways. In some villages the baker really makes a ring or a hole in the middle of the dough piece while in others a kind of dimple is made in the middle of the product. So, the practice of making a ring-shaped product is not confined to American bakeries. This form of bakery shape has existed in Belgium since the Middle Ages. People used to take the mastellen to the church so the priest could bless them. They were supposed to be a good remedy against rabies. After proofing they are brushed with egg and baked for about 10–12 min in a hot oven (200 °C).

Brazil

The most famous speciality of Brazil is without doubt *pão di queijo* or cheese bread. One wonders whether this product can be called bread because it is made from cassava flour. Nevertheless because the product is such a delicacy and is made by all bakers in Brazil it must be included in the list of the world's specialities.

There is also no yeast in the formula and the increase in volume is due to the development of steam within the product during baking. This is similar to the process and the volume increase when baking choux paste. The product has a short shelf life and is normally eaten immediately after baking. In Brazil the baker uses *queijo de Minas* (cheese from Minas), which is rare in other parts of the world. However, the product can be made with a mixture of Parmesan and Cheddar cheeses.

Pão di queijo originates in the province of Minas Gerais and is served in nearly every restaurant with every type of meal. Actually, the original product did not even contain cheese. In the 17th century, the slaves of the rich landlords made a kind of cooked "starch balls" from cassava flour and used this as their staple food. It was about 200 years later that people started adding milk and cheese.

There are also two types of cassava flour (called *polvilho* in Portuguese), one sweet and the other sour. Both start from the flour of cassava (or yucca) root mixed with water. The sour type is obtained by the fermentation of the water solution by lactic acid bacteria. Afterwards the slurry is dried and the result is sour polvilho (Bertolini and others 2001).

The recipe for pão di queijo is as follows: polvilho (100%), eggs (50%), skimmed milk (25%), grated Cheddar (25%), sunflower oil (22%), Parmesan cheese (6%), salt (1.2%). The first step in the preparation is to boil the milk with the oil, slowly and gradually add the cassava flour in order to obtain a homogeneous mix. Cool to lukewarm. Add the eggs and mix to get a pliable elastic dough. Finally, add salt and cheeses.

Divide the dough into pieces of about 25 g, shape into round balls and brush with some oil. Bake the dough at 180 °C for about 10 min until the product becomes pale yellow. The breads should not become too dark or crusty. This is a slightly colored pale product, not crusty but soft. The Cheddar will also impart a yellowish colour.

China

Lao bing is flat bread made from weak wheat flour (8.5% proteins, 10% maximum). So this product is actually made from cake flour rather than from bread flour. Lao bing contains only three ingredients: flour (100%), water (10%), and salt (2%). The dough is prepared with water < 30 °C.

After mixing the dough is covered with a moist cloth and allowed to rest for about 30 min. After resting, it is divided into small pieces of about 30–40 g each, which, after another short rest of about 15 min, will be laminated and shaped, about 13–17 cm wide by 23–26 cm long. After laminating, the dough pieces are amply brushed with peanut oil and rounded again. After another 15 min rest period, the dough pieces are again laminated in the shape of pancakes and baked in a pan. During baking the bread is turned over frequently in order to bake it evenly on both sides.

Finland

The people from Finland have the same relation with rye bread as Popeye has with spinach. "Crispbread" is a part of the daily menu in Finland. Everyone in Finland is convinced that rye bread "keeps a man healthy, wealthy and wise". As with most rye bread, the use of sourdough is essential.

Traditionally, Finnish sourdough is made from rye flour and *viili*. Viili is a fermented milk product. Fermented milk plays an important role in the daily diet in Scandinavia. A lot of people produce sour milk products in their homes. Because of the cold climate, fermentation normally uses mesofile starter cultures, especially those with lactic acid-producing lactococci. Viili is a thick, slimy, sour milk product made from whole milk. Microbiological analysis shows that many different kinds of lactic acid bacteria are present in viili. *Lactococcus lactis* subsp. *cremoris* and *Lactococcus lactis* subsp. *lactis* are responsible for the consistency of the product while the flavor is imparted by *Lactococcus lactis* subsp. *lactis* var. *diacetylactis, Leuconostoc mesenteroides* subsp. *cremoris* and *Leuconostoc mesenteroides* subsp. *dextranicum*. Another property of viili is that it also contains a mold called *Geotrichum candidum*, which causes the formation of a small amount of alcohol. This mold lowers pH and produces carbon dioxide in addition to alcohol.

Another characteristic of sourdough production in Scandinavia (and Russia) is boiling the flour–water slurry as a first step in the process. This kills the background flora and, at the same time, gelatinizes the starch in the flour, making the starch more readily available for the lactic acid bacteria. This technique has become increasingly widespread in Europe. In Germany, the process is called *Kochstuck* and the final fermented sourdough is called *Aromastuck*. Sometimes the water is replaced by beer which has been left open to remove all carbon dioxide.

A well-known bread in Finland is *ruisleipa*. The first step in its production is the preparation of the sourdough as follows. Boil a mixture of 125 g rye flour and 125 g water for about 3 min. Allow to cool to room temperature and add 50 g of viili. Leave to ferment for 24 h at ~8–12 °C (not in the refrigerator!). Boil 125 g of beer and 125 g of rye flour. Cool and add the mixture to the sourdough. Leave for another 24 h in a cool place. Cover with a plastic sheet.

On the third day, make the bread with the following recipe: wheat flour (100%), sourdough (100%), rye flour (65%), water (55%), butter (5%), yeast (2.5%), and salt (1.8%). After mixing, divide the dough in equal portions of about 400 g. Let it rest for 30 min and shape the dough in to disks about 3 cm thick and 20–25 cm diameter. Make a hole in the middle of the disk. Proof for 2 h and bake at 200 °C for about 30–35 min.

Another speciality of Finland is called *pulla*, a soft sweet roll made from wheat flour. Ingredients such as cinnamon, cottage cheese, lemon peel or dried apples can be added to the basic recipe. The composition of the basic dough is: wheat flour (100%), milk (50%), butter (25%), eggs (10%), sugar (5%), raisins (5%), yeast (5%), salt (2%), and cardamom (0.5%). Beat the eggs together with the sugar. Add milk, salt, yeast, and cardamom, and mix. Then add about three-quarters of the flour and mix until homogeneous. Add the rest of the flour and mix to a smooth elastic dough. Add the butter and mix until the dough breaks loose easily from the sides of the mixing bowl. Cover and allow the dough to double in volume. Mix

again and add the raisins. Divide the dough in to 1 kg pieces and shape into rings. Leave to ferment for 90 min. Brush with egg yolk and bake at a moderate temperature. After baking, brush with sugar syrup and decorate with almonds.

France

France is the country of the baguette. Of course, when one travels from Lille in the north to Nice in the south, one finds many types of baguettes. Though the French talk about a baguette or a *parisienne*, or *le pain briare*, there is quite a lot of difference between the baguettes from the different regions in France.

To make a traditional baguette, the baker normally uses malt. Pain briare is made of wheat flour, gluten, rye flour, salt, sourdough, malt, and ascorbic acid. The dough is prepared with lots of water (up to 80% of flour weight) and a little yeast (maximum 1% of the flour). The dough rests in a bowl for about 1 h and is scaled into 320 g pieces and given a first proof of another hour. Finally, the dough pieces are molded into the typical long shape and have a 1 h final proof.

There is a big difference between a baguette and a pain briare. The latter has a hard dark crust and a glassy brownish irregular crumb structure. A baguette, on the other hand has a white crumb with a regular structure, a few bigger cells, and a thin shiny golden crust.

Each baker in France still knows the method to make tasty bread and will use sourdough or "poolish" in order to get the typical "taste." The small baker in France is also distinguished by a quality of products that is recognizable. In France, the expression *pain maison* (bread of the house) is protected. "Don't buy your daily bread just anywhere, buy from the artisan baker" is the well-known slogan.

In France people also eat other types of bread of course. A well-known one is *la boule* (literally meaning the "the ball" or "the bulb"). It has a long shelf life and is made with sourdough. For each kilogram of flour, 400 g of sourdough is used, 3 g of yeast and about 0.650 l of water. A long fermentation process is involved: floor rest of 1 h, an intermediate proof of 1 h, and a final proof of 2 h. In France, sourdough bread may not contain more than 3 g of yeast/kg flour.

Baguettes are traditionally made with little yeast. The dough will get enough time to mature and to rise. However, even the French baker increasingly uses so-called "bread improvers". In combination with these chemicals, the baker uses more yeast and ascorbic acid in order to "tune up" the bread. As a result the baguette has lost its original "goodness". Fortunately there has been a counter movement and *pain tradition* is now a protected trademark in France. Only when the baker makes the bread according to a strict set of rules (such as the use of sourdough, little yeast, and no ascorbic acid), can it be called pain tradition. It also has to be baked on the floor of the oven. A bread baked on a baking tray in a rack oven can be easily identified because it will have the typical pattern of small holes from the baking tray.

Germany

Germany is well known for its rye bread, although there are other countries where rye bread is as popular as wheat bread. Rye bread is very popular not only in the Scandinavian countries but also in Poland and Russia. The steps to make rye bread are essentially the same as those for making wheat bread. However there are major differences in the production method.

Sourdough is a mandatory basic ingredient in making rye bread because rye does not contain sufficient gluten to produce a well developed gluten network as one obtains with wheat flour, which is responsible for the water-binding and gas-retaining features of a wheat dough. In a rye bread, these functions have to be performed by pentosans which are abundant in rye. Under low pH, the ability of pentosans to dissolve in and absorb water is greatly enhanced.

The dough is acidified using sourdough. Due to the low pH, enzyme activity is inhibited, enhancing the water-binding capacity of starch. As a result, the volume and the crumb structure of the rye bread are improved. Acidification also helps to extend the shelf-life of the product. A low pH inhibits the growth of spoilage microorganisms. Also, the nutritional value is enhanced by the acidification, as the minerals present in the bread will be more readily assimilated in the human body. Finally, sourdough also contributes to the flavor of the bread (Siebel and Weipert 2001).

More water is used when making rye sourdough than in making wheat sourdough. Mixing is also less intensive then that for wheat dough as there is no gluten network to be formed and developed. The water absorption by the pentosans occurs quickly and easily. Hence, the use of intensive mixers is not necessary to make a good dough for rye bread.

Mixing times are influenced by several factors, with the most important ones presented in Table 38.1.

Table 38.1 Factors that influence mixing time

Short mixing time	Long mixing time
High-speed mixer	Slow traditional mixer
The higher the percentage of rye flour	The higher the percentage of wheat flour
Weak flour	Strong flour
Low bran content	High bran content
Particle size of flour: fine flour	Particle size of flour: coarse flour
High dough temperature	Low dough temperature
Low water content of dough	High water content of dough
Indirect mixing (autolysis)	Direct mixing

It is obvious that all rules of good manufacturing practice also apply to rye bread, for example, the importance of correct scaling, and the rigid control of humidity and temperature. Furthermore, it is important that the sourdough is fully matured.

When indirect mixing is applied (adding or production of sourdough in various stages), a bowl rest after mixing is not required. If rye bread is made using direct mixing, a bowl rest of

20–50 min is necessary. However, the length of the bowl rest depends on the percentage of wheat flour used in the dough.

After mixing and floor rest, the dough is divided. Again, it is important that all individual pieces have about the same weight and shape to ensure a smooth and regular baking process. There is also a legal consideration. In countries where the weight of a loaf of bread is legally determined, scaling has to be checked regularly as the specific weight of the dough will change during operations.

After scaling, the dough pieces are allowed to relax for 10–20 min and then molded into their final shape, which can be round, oval or sausage-like to make tin bread. The equipment used to divide and mold rye bread is totally different from the equipment used for wheat flour. During these operations relatively large amounts of dusting flour are required because rye doughs are stickier then wheat doughs.

After molding the breads are put in baskets or baking tins and allowed to rise. If a short final fermentation period is desired, the proof temperatures will range from 35 to 40 °C instead of the more common 25–30 °C. With the short fermentation time, relative humidity should not be too high and a range of 60–65% is adequate. With longer fermentation time it is better to choose a relative humidity of 80% or slightly higher.

It is common to choose a slow fermentation process. Aside from the lower temperature, the dough will be a little more consistent and less yeast will be used. The fermentation process of rye bread should be carefully monitored. Rye doughs are less tolerant then wheat doughs, and errors that occur during fermentation will easily and immediately have a negative effect on the quality of the final product (Meuser and Brümmer 1994).

For the baking process, the same principles apply as for wheat dough. In other words, baking times depend on the shape of the bread (time necessary to reach 100 °C in the centre of the bread), and not on the weight of the bread or on the baking temperature. There is water migration towards the centre of the loaf, and all phenomena take place simultaneously in different spots in the crumb, depending on the temperature of that spot; therefore crust characteristics are determined by baking temperature. Baking time is longer for a rye bread then for a wheat bread due to the rate of heat transfer within the crumb. Generally speaking, Table 38.2 can be consulted as a rough guide for baking times for rye bread. In this table "rye + wheat" means that the percentage of rye in the dough is higher than the percentage of wheat, while "wheat + rye" indicates a reverse situation.

Table 38.2 Baking times for rye bread

Weight (g)	Type	Temperature (°C)	Baking time (min)
500	Rye + wheat	210–260	35–40
500	Wheat + rye	180–230	30–35
1000	Rye	220–270	55–65
1500	Rye	220–270	65–90

Greece

A very well known speciality from Greece is *tsoureki*. It is a rich recipe type Danish pastry (but not laminated) with lots of eggs, butter, and milk. It is mainly consumed around Easter and a real traditional tsoureki will be decorated with boiled eggs that are painted red. The product, however, is available all year round, without the egg, as a morning roll (of about 50 g).

The composition of the dough is the following: flour (100%), milk (33.3%), eggs (22.2%), butter (11.1%), sugar (10%), yeast (5%), salt (2.2%), mahleb (1%), and cinnamon (1%).

Separately mix the flour, the salt, the mahleb, and the cinnamon. Make a slurry of the yeast, using some of the milk. Mix sugar and butter and then add the eggs until smooth. Add both mixes to the flour mix and knead to a homogenous elastic dough. Brush the surface of the dough with sunflower oil and cover with a damp cloth. Leave to ferment for 1 h. Degas and leave to ferment for another hour. Divide the dough into pieces of about 500 g, mold in the shape of a sausage and make a plait with 3 dough strings, thus making breads of 1.5 kg. Leave to prove for an hour and brush the surface of the dough with a mixture of egg and water to which a little honey has been added. Decorate with flaked almonds and bake for 35−40 min at 190 °C.

Hungary

Vazsonyi is a typical speciality from Hungary. Originally it was made on the farms in small villages, but nowadays it can be found in most bakeries in Hungary. Typical ingredients are wheat flour, rye flour, and mashed potatoes. The following recipe can be used to make this delicious product: wheat flour (100%), water (65%), rye flour (11%), mashed potatoes (3%), salt (2%), and yeast (1.5%).

This product is made with a sponge-and-dough method. A sponge is made using all of the rye flour, three-quarters of the water, one-third of the flour, and one-third of the yeast. The sponge is allowed to ferment for 5–7 h at room temperature. Afterwards, the rest of the ingredients are added and mixed until a smooth dough results. After mixing, the dough is immediately divided into 520 g pieces.

After rounding and proofing of the dough pieces, the bread is baked for about 25–30 min at 200–220 °C. This will produce a product that stays fresh for quite some time, and the staling process will be slow. This is due to the presence of the mashed potatoes, which contain mainly starch. Potato starch, however doesn't have the same staling pattern as wheat starch, and therefore the product will stay moist and soft for longer.

The addition of mashed potatoes is a technique that was widespread in Europe after World War II, when there was a shortage of wheat flour. Today, the mashed potatoes can be replaced by potato flakes which are readily available in the supermarket.

India

Chapati is a typical flat bread that can be found everywhere in India. The recipe is simple. The product is easy to make and can be prepared quickly. It has to be consumed very straight after making because it stales very quickly.

To make chapati you need wholemeal flour (100%), water (60%), and salt (2%). Sift the flour and set some of the bran aside. Add half of the water and the salt. Mix and gradually add the rest of the water until an elastic dough is formed. The dough should be slightly moist. Divide the dough into small pieces and roll them into the rest of the bran and some flour. Leave to rest for a couple of minutes and make disks of about 170 mm diameter. Heat a frying pan without butter or oil and bake the chapati for about 30 s either side. Turn the chapati over and bake again for 30 s. Repeat this until the chapati is well baked (Faridi 1988).

Naan is another well-known product from India. To make it you will need the following ingredients: flour (100%), yoghurt (26.5%), milk (22%), eggs (11%), sesame oil (11%), sugar (6.6%), yeast (5.5%), salt (1.5%), and sesame seeds (1.5%).

To 50 ml of lukewarm milk, add 5 g of sugar and all of the yeast. Mix to a homogenous yeast suspension. Take care not to warm the milk too much.

Heat the yoghurt to about 60 °C to inactivate the lactic acid bacteria present in the yoghurt. Add the rest of the sugar, the milk, the eggs, the oil, and the salt and mix. Add the flour and the yeast slurry. Mix to make an elastic homogeneous dough. Leave 2 h to rise and mix again. Divide into equal portions of about 100 g and shape into disks of about 200 mm diameter. Brush with sesame oil or melted butter. Decorate with sesame seeds or with other kind of seeds such as onion seeds. Bake in a preheated oven at 230 °C until golden brown.

Pappadam is a bread made from lentil flour and is as thin as a pancake. It looks a bit like a tortilla but it is not soft, it is baked dry like a cracker. Sometimes it contains all kinds of spices and herbs, but in the south of India it is produced without spices. In the northern parts of India, red peppers or garlic are added. Sometimes the dough is baked in a pan, sometimes it is grilled.

Ireland

Barmbrack is normally made with yeast but there are also recipes which call for baking powder. It is a typical Irish bread normally sold during the time of All Saints. There is also a similar product in Scotland. The uniqueness of this product is the raisins and the orange peel which are allowed to soak overnight in tea.

To make this delicious product you will need the following ingredients: wheat flour (100%), milk (55%), raisins (33%), currants (33%), orange peel (7.5%), butter (5%), sugar (5%), yeast (3%), salt (2%), eggs (1%), ginger (0.5%), and nutmeg (0.1%).

Add the yeast to the milk and make a suspension. Mix the flour, salt, sugar, ginger, and nutmeg. Add the yeast suspension, then the butter and the eggs. Knead until smooth and elastic. At the end of mixing, add the raisins, currants, and orange peel. Divide in pieces of about 500 g and shape into cylinders. Put in a buttered bread tin. Leave to proof for 1 h and bake for about 45 min at 200 °C.

Italy

A well-known speciality of Italy is *focaccia*; however, there is such a vast choice, that it is impossible to describe all types. Each region, yes, nearly each village in Italy has its own focaccia. Sometimes the Italians will call a focaccia, a *pizza bianca* or "white pizza", indicating that the product is similar to a pizza but without tomato sauce. Usually it is much thicker than a traditional pizza from Napoli. A real pizza is only a couple of millimeters thick, with variations at different fast food chains. A focaccia, on the other hand, can be 3–4 cm thick. As result you will find it more often cut in two halves, which are then decorated with all kinds of nice things such as olives, Parma ham, mozzarella cheese, garlic, and so on.

Then there is the *ciabatta*. This is bread made with a slack dough containing about 65–70% of water to flour and 3–5% of olive oil. After mixing, the dough is allowed to ferment in the mixer for 90–120 min. Afterwards it has to be treated very delicately to maintain the gas bubbles in the dough. The baker gently laminates the dough and cuts rectangular pieces of about 250–300 g measuring about 10 by 20 cm. These dough pieces are allowed to ferment for another 90–120 min in a dry proof box (not more than 60% relative humidity; Italian bakers don't mind that the dough crusts a little). After about three-quarters of the proof time the baker will pull the dough until the piece is about 30 cm and turn it over so the dry side lies underneath. This handling is called *stirare* in Italian, and literally means "to iron". It is due to this treatment that the product gets its typical ciabatta shape. Although ciabatta means "slipper", the product actually looks more like a dog bone with an irregular cracked crust.

Together with the irregular open crumb structure showing big shiny holes, a thick crust is typical for a good ciabatta. A ciabatta is by definition always baked on the oven floor and the author is convinced that the crust is one of the reasons why this product became a worldwide success so quickly. As more products are now baked in a ventilated hot air oven, the crust of many products, such as baguettes or croissants, resemble each other. The goodness of bread baked on the oven floor has been rediscovered in ciabatta.

Japan

A typical and traditional homemade Japanese product is *saka-manju*. Nowadays it is made on an industrial scale with various fillings such as red bean paste, meat, and so on. A peculiarity of this product is that it is not baked in a traditional oven: after fermentation, the product is steamed, as rice is steamed in Japan. Steam baking is common in Japan.

The composition of the product is usually as follows: flour (100%), water or milk (50–55%), yeast (2–3%), sugar (5–10%), lard (3–5%), and salt (0.5%).

The yeast is dissolved in lukewarm milk together with the sugar. The mixture is added to the flour and mixing is started. During kneading, the salt and the melted lard (not hot but just liquefied) are added to get a stiff dough.

The dough is rested in a bowl until it has doubled in size and then it is mixed again. At that moment the dough will be molded in to a "sausage" shape and cut into slices about 2–3 cm thick. The slices are flattened. The filling is placed on the dough disc, which is then closed so the filling sits in the middle of the dough. The product is given a short proof time (about 10–15 min) and then steamed.

Sometimes sake, a beverage made from fermented rice, is used instead of yeast. Steaming is an interesting technique, and there are many different types of steamed breads in Japan. They all have the following common characteristics: large volume (2.5–3 times as big as the non-steamed product); shiny white crust (because of the steaming, no Maillard reaction can take place); and elastic, resilient crumb which does not stick to the teeth on mastication.

Mexico

Anyone who says Mexico thinks of *tortillas*. Tortillas look like thin pancakes made from bread dough. They are normally filled with meat and beans and then folded or rolled. It is therefore very important that the tortillas are soft and pliable. Tearing while they are being rolled is considered to be a product fault.

Originally the product was only made in the north of Mexico. Today it is readily available in the south of the United States and throughout Central America. Tortillas are made at home and are supposed to be consumed within one day. Today with the use of emulsifiers, they can be kept for 3–5 days, especially when they are kept in the refrigerator. It is important to store them in a cool place to avoid spoilage by mold growth.

Tortillas are made with flour with a high protein content. Apart from flour (100%), the dough contains water (40%), margarine (12%), and salt (2%), a simple recipe, without yeast. After mixing, the dough is divided into pieces of about 20–30 g that are allowed to rest for about 15 min. Afterwards they are laminated into round flat pancakes of about 12–15 cm diameter. The thickness varies between 2 and 5 mm. Baking is done on a hot plate (not in a traditional oven) at about 200 °C. After 15–20 s, depending on the thickness, the product is turned over. The other side is allowed to bake for another 10–15 s.

In Guatemala, a totally different recipe is used: flour (100%), water (44%), sugar (25%), eggs (4.5%), oil (4.5%), and salt (2.5%). For everywhere else, tortillas are made in the same way as described earlier.

New Zealand

Rewena is Maori bread made with sourdough. The sourdough is made from potatoes. As mentioned earlier, the use of mashed potatoes in bread is not unusual and in Belgium, , when wheat was scarce just after the World War II, bakers used to add potatoes to the dough. The Maori sourdough is composed of three medium-sized potatoes, 250 g of flour, 235 g of the water in which the potatoes were boiled, and 15 g of sugar.

Allow the potatoes to cook well. Separate the water and the potatoes and allow both to cool to room temperature. Mash the potatoes and add the flour and sugar. Finally add the water. Cover and allow to acidify at room temperature for 48 h.

To the sourdough, add 750 g of flour, about 400 g of water, 30 g of yeast, and 20 g of salt. Mix until smooth and homogeneous. Add some more water if necessary. Leave to ferment for 30 min and divide the dough into 250 g pieces. Shape into a disk. Brush with sunflower oil and leave to proof for 1 h. Bake at 160 °C for 30–35 min.

Pakistan

Puri is quite similar to chapati bread from India. The following recipe can be used to make puri: flour (100%), yoghurt (22.2%), sesame oil (11%), sugar (6.6%), salt (1.5%), and pepper (0.4%).

Mix all ingredients until a smooth and elastic dough results. Leave the dough to rest for about 10 min and divide it into pieces of 40 g. Shape the individual pieces into pancakes. Heat oil in a baking pan and bake the puri about 1 min either side. Serve hot.

Poland

Babka is a typical product from Poland of which many different kinds can be found. Certain types are made at special occasions such as Easter or Christmas. The following recipe is for the Easter babka.

You will need flour (100%), milk (37%), butter (37%), egg yolk (20%), raisins (15%), sugar (15%), yeast (5%), orange peel (3%), and salt (2%).

Mix all ingredients, except the raisins and the orange peel, until you get a smooth elastic dough. Add some extra milk if necessary. Cover the dough with a damp cloth and leave to rise until double in volume. Add the raisins and the orange peel and mix until they are homogeneously distributed throughout the dough. Divide into 550 g round pieces. Put the dough pieces in a well-greased round baking tray. Leave the dough to rise for 1 h and bake at 190 °C for 35 min. Cool the babka and decorate with icing sugar.

Sweden

Limpa is a dark rye bread which is normally served with smorgasbord. It is quite sweet because of use of the brown sugar and molasses. But in combination with the salty, savory smorgasbord, it is a real treat for your taste buds.

Limpa is made with the following recipe: flour (100%), water (85%), rye flour (65%), broken wheat kernels (15%), molasses syrup (10%), butter (10%), buttermilk (6%), yeast (3%), mixed peel (1.5%), aniseed (0.5%), and flax seeds (0.5%).

Mix the wheat kernels with the aniseed, flax seeds, salt, mixed peel, and molasses syrup. Boil the water and add it to the mixture. Leave to cool, stirring occasionally. Add the butter followed by the buttermilk, rye flour, and wheat flour and add the yeast last. Mix until smooth but stiff. Divide in 525 g pieces and shape into ovals. Leave to proof for 2 h, degas and shape again into an oval piece of dough. Leave to rise for another hour and bake for 35 min in an oven at 180 °C.

Turkey

In Turkey bread is called "the food of friendship". Bread is treated with respect and it is regarded as a sin to throw bread away. However, if bread is too old and has to be thrown away, Turkish people, before doing so, will kiss it and touch it with their foreheads. Only then will it be thrown away. However, Turkish housewives are masters at using old bread, which may be added in little cubes to a typical soup, *köyçorbasi*. Or, the bread may be moistened with water and oil and then roasted. Or, the bread may be mixed with vinegar and garlic to make *sarmisaklisos*, which is normally eaten with fried fish.

In Turkey there are many varieties of bread, of which most are flat. Note that the origins of bread are expected to be found somewhere in the flatlands of central Asia. The most traditional bread in Turkey is *yufka*, a paper-thin bread made from unleavened dough (Faridi 1988). Even today you will find anywhere in Anatolia women who make this type of product using an *oklava* (roller). These breads, like most thin breads, are not baked in an oven but on a hotplate. Actually, a similar dough exists in Greece: *phyllo* dough. This is puff pastry that, after lamination, will be stretched so far that it becomes thin enough to read a newspaper through the dough.

The best-known bread of Turkey is the *pide*, a flatbread which has many variations such as *Karadenizpidesi, helvapide* (which originated in Bursa), and the *Ramazanpide*, just to name a few. Pide is a big, flat (2–3 cm thick), soft bread that is used to dip into all kind of sauces, olive oil, or yoghurt. It must have a fine regular crumb and a thin crusty crust. It is normally baked in a hot oven for a short time. Before baking it can also be decorated with all kinds of things such as sun-dried tomatoes or olives. In that way it becomes similar to a pizza. As a matter of fact, Turkish pizzas are delicious.

To make pide you will need the following ingredients: wheat flour (100%), water (35%), melted butter (10%), yoghurt (5%), sugar (3.5%), and yeast (3.5%). The dough is mixed well until an elastic product results. The dough has a floor rest until it doubles in volume. After degassing, the dough is divided into pieces of about 350 g. After a short resting period of about 15 min, the dough pieces are shaped into disks which are allowed to ferment for another 15 min. The dough is baked for about 10 min, depending on the thickness of the disks. A couple of minutes before the end of the baking time, the bread is removed from the oven and quickly brushed with melted butter and decorated with sesame seeds. The bread is then allowed to bake for another 2–4 min.

United Kingdom

Many people have expressed dissatisfaction with the bread in England. Luckily, it always gets toasted. The United Kingdom is a clear example of what happens to the quality of bread when commercial bakers replace small artisan bakers. Big bread factories are more concerned with competition than with the quality of bread. This is compounded by the tendency of retail chains always to be looking for a cheaper product. This results in a situation in which products of poor quality are sold at a ridiculously low price.

This phenomenon can be observed in countries such as the United Kingdom, the United States, and the Netherlands, where the small baker has almost completely disappeared. In other countries, such as Switzerland, Belgium, and Italy, where the small baker is still holding a strong position, the industrial baker is forced to use the artisan baker as a benchmark. Thus, even an industrial baker is producing excellent bread, with efficiency and adequate hygiene.

England, however, has two products, which in the strict sense, are not really bread but which are worth mentioning. These are scones and muffins. For the younger generations in America, muffins (and pizzas) are of American origin. Muffins are as English as the Queen and the term *English muffins* should settle all disputes.

Let us first have a look at scones. It is interesting to note that the word "scone" derives from a Dutch word namely *scone* or *skone*, that is, "nice". So scones literally mean "nice little bread". The reason for the name was not that the product was beautiful to look at: in the Middle Ages, it was called "nice" because all kinds of ingredients such as honey, raisin, and nuts were added. Scones are made with baking powder.

If you want to try to make pumpkin scones yourself, you can use the following recipe: flour (100%), pumpkin puree (100%), sugar (50%), eggs (25%), butter (7.5%), salt (2.5%), and baking powder. The quantity of baking powder depends on the type you use.

The first step in making scones is to mix all dry ingredients. Cut the butter in small cubes and mix them into the mixture. Gradually add the liquids (eggs) and the pumpkin puree. If needed, a little milk can be added to make a smooth but dry dough. Laminate the dough into a sheet of about 25 mm thickness and cut round pieces of about 50 mm diameter out of the sheet. Bake the scones for about 15–20 min at 220 °C.

Muffins are simply cakes that are very fluffy and light. There are numerous varieties. The most popular one seems to be the blueberry muffin, but apple and spice and double chocolate are of course also real delicacies. A recipe for almond muffins uses flour (100%), milk (33%), sugar (33%), sunflower oil (23%), broken almonds (20%), eggs (16%), salt (1.5%) cinnamon (0.5%), and nutmeg (0.3%). Again, the quantity of baking powder used depends on the type of baking powder.

Mix all raw materials and beat in order to obtain a smooth batter. Divide into paper cups and bake for 10–15 min at 200 °C.

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39
Bakery Products of China

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Brief history of baking in China

China, as one of the world's four greatest ancient civilizations, is famous for its early technological advances in ancient times. Compared to the invention of, for example, explosives and printing, the advances in food preparation are less well-known. Starting with Emperor Yan 炎帝/*Shen Nong* 神农 (about 4000–5000 bc), the first ancestor of the Chinese who tried out hundreds of plant materials, the growing of grains, edible plants and medicinal materials was introduced to the general population, followed by the development of a structured and systematic farming culture, which subsequently formed the basis of the Chinese civilization (Pang 2009). When it comes to food, the Chinese have a common saying: "The masses regard food as their God", which indicates how important food is in people's minds. For a long time in Chinese history the eating of food was not just to fill the stomach, but had a significance that was far beyond this. Being able to consume a good amount of food, and eat foods for the purposes of both well-being and medication is rooted in Chinese society, and is a significant part of Chinese culture. The enormous variety of delicious foods prepared by cooking in China is perhaps very hard to match anywhere else in the world. Like the cuisine of France or Italy, which are well-known around the world, Chinese cuisine has superb reputation (Liu 2004).

It is unquestionable that China is a gourmet food paradise. Among countless delicacies in China, the delicate traditional baked foods are significant and play a very important role as either staple food or non-staple food. From the perspective of nutrition, cereal grains are the most important human nutrient source. Hence the history of cooking culture is directly related to the history of wheat cultivation. From a social perspective, the development of a catering culture is an important part of the evolution of the human race. Thus, the preparation and baking of wheat-based food represents the foundation of human cooking culture coupled with technological development (Li 2002). According to an American anthropologist, wheat was first used as a food crop 17 000 years ago; and wheat was first cultivated by the Chinese about 5000 years ago during the time of *Shen Nong* 神农 (the legendary father of agriculture). At first, the grains were eaten raw, but soon the art of grinding into flour was learned. There is a reference in the Old Testament that bread was not leavened as early as the Israelite exodus from Egypt. It was much later that scientists discovered that bread was leavened by the action of tiny airborne microorganisms, known collectively as yeast. Even though wheat is a staple food grain in the West, the Chinese have developed many more ways to prepare it (see Figure 39.1). This very wide variety of Chinese grain products, and their level of sophistication, is due to the many different methods of preparation and cooking that have been developed, including frying, deep frying, baking, steaming, and boiling. Dishes can be sweet, salty, soft, hard, crispy, spongy or flaky (Sinorama 1984).
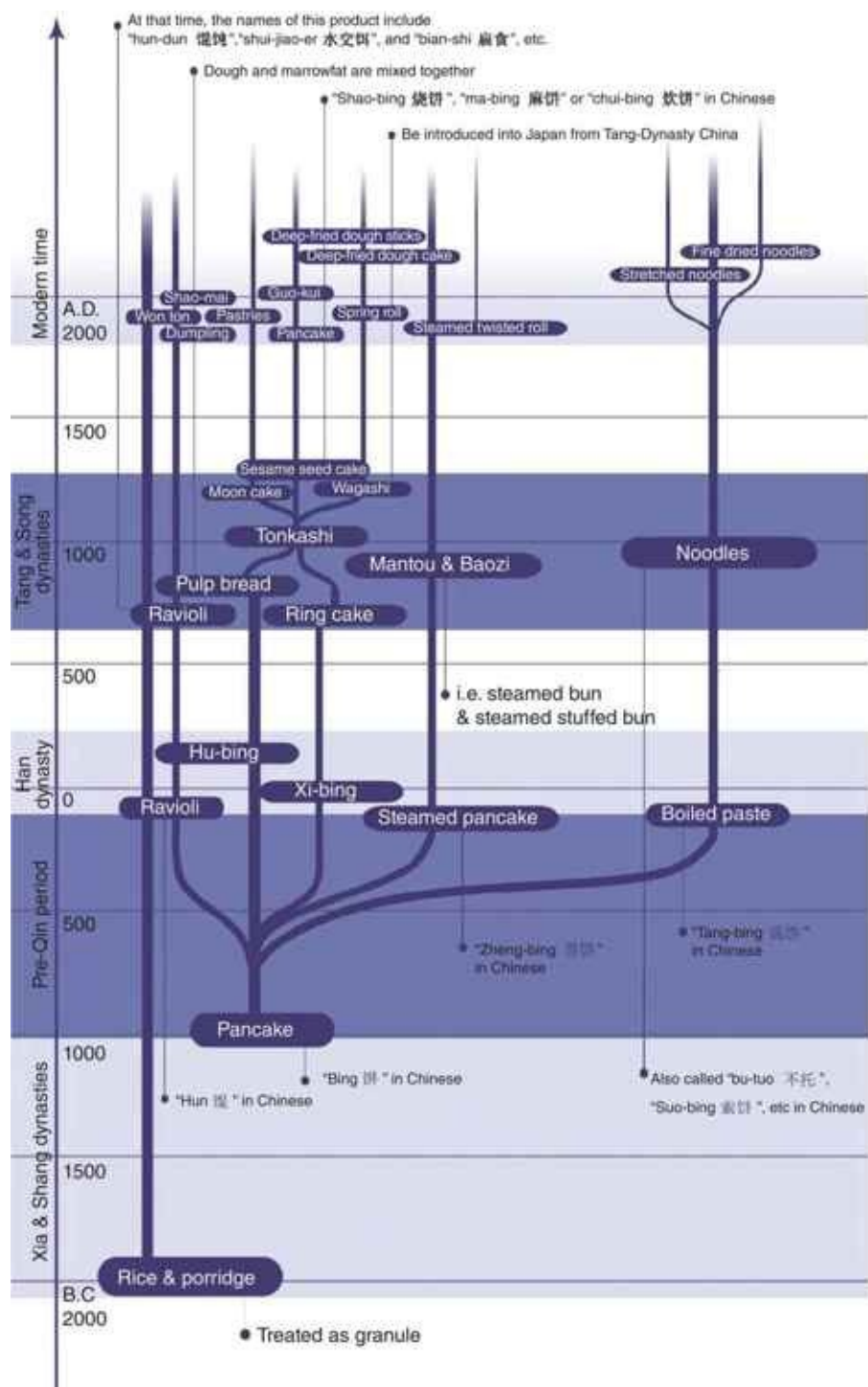
Figure 39.1 An illustration of the evolution of wheat products in China.

From the outset, wheat was pulverized and mixed with water to make a simple paste, which was then baked in an earth kiln. The finished product was like a thin pancake which was hard and crisp. Dough made out of wheat flour appeared in the late Warring States period (475–221 BC). By the time of the Han Dynasty (202 BC to 220 AD), a generic term "*Bing* 饼" had appeared, and was used to refer to various kinds of baked dough products such as flat bread, buns, dumplings, baked cakes, and noodles (Sterckx 2005). There have been a number of documents produced in ancient China recording early civilization, including more specifically, the technologies or principles of wheat food manufacturing. For instance in *Li Ji* 礼记 (the Book of Rites – the exact completion date of this book is debatable), it is said that the ancient Chinese people fried grain and baked meat as foods before the process of steaming was developed. In addition, in the Book of Zhou (636), notes that Emperor Huang started to steam grains to make meals, and boil grains to make porridge, utilizing an ancient earthen

utensil called a "*Zeng* 甑" (Li 2008). Moreover, China was one of the world's leading civilizations in terms of fired ceramics and smelting technology; bronze and other metalware were used for cooking utensils. Additionally, wheat and grains were processed into staple foods in the form of granules, which contributed to the formation of the unique cooking culture of China. Compared to grilling and broiling technologies, stewing and steaming methods have their obvious superiorities. Specifically, stewing and steaming methods avoid the shortcomings of grilling and broiling, such as the massive loss of nutrients and the generation of potentially harmful carcinogens during the process, as well as improving cooking efficiency. In contrast, Western cultures have currently not used steaming methods nearly as much, and the word "steamer" usually refers to a steam engine or steam-driven boats.

When it comes to cooking methods, the ingenious use of steaming, boiling, baking, and frying technologies can be adapted to different manufacturing requirements. The evolution of wheat-based food in China is illustrated in [Figure 39.1](#), and refers to the examples that have been mentioned in ancient Chinese books (Li 2002). For making steamed bread "馒头", it is seen that the application of fermentation is required in food preparation. The invention of dumplings and wonton was the pioneering work of the Chinese ancestors of those of today, for both the food nutrition requirement as well as the sensory/texture requirement. Furthermore, *Baozi* 包子 was invented as a fast food 1000 years earlier than the hamburger. To sum up, bakery products, including wheat products, have not only contributed to part of the Chinese identity, but have also made great contributions to the diet of all the cultures of the world (Li 2002).

Main baking technologies

Bakery products in China can be divided into two types: staple foods and pastries. In the past, most of the bakery foods in China were completely handmade. Today, the breads which are rectangular in shape and are similar to those consumed in the West, are usually made with automated equipment. Many cakes are also increasingly made using automation. For many traditional product types, however, final product quality is still largely controlled through experience and high-level craftsmanship rather than engineering principles. There may be many reasons for this, but in particular, Chinese people have long regarded the consumption of exquisite foods as one of life's main pleasures. Cooking is more like art than like science and technology. Besides, academic study of traditional empirical approaches has been limited, resulting in a general lack of deep mechanistic understanding of the details of the traditional processes. In the following sections, the traditional technologies of the manufacture of Chinese bakery products are briefly introduced.

Baking

Like many other countries comprising a vast territory, dishes in Northern and Southern China differ according to the climate and geography (Sinorama 1984; Liu 2004). Much of Northern China is too cold or too dry in winter to support rice production, so the main crop there is wheat. Some Chinese minority groups, for example the Uighur in the West of China, use wheat to make breads which may be called "*Nang* 馕 ", but most Chinese use wheat flour to make steamed dumplings and noodles (Roberts 2002). It has long been observed that Northern Chinese people eat baked wheat cake, baked pancake, and *Guokui* 锅盔 (pan-shaped pancake) as their staple foods. These traditional foods with Chinese characteristics are all prepared and then baked, and these products have their own unique tastes and wholesome flavors. One amazing example is the Moon cake, which has won fame both at home and abroad as a festival food of China, used to celebrate a day when family members get together under the full moon.

Baking ingredients

Although there is a great variety of traditional baked foods in China, they can be divided into two groups: fermented, such as Nang, Shaobing 烧饼 , and Guokui; unfermented, such as pancake and *Laobing* 烙饼 , respectively. The main ingredients of fermented products are flour, water, salt, fat, and yeast. Furthermore, sometimes soda (dietary alkali) is added to neutralize the acid produced in the fermentation process. In contrast, unfermented products are made using batter, which is a semi-liquid mixture of flour, water, and other ingredients such as corn starch, durra flour, and yam starch.

Principles of baking, and equipment

Qimin yaoshu 齐民要术 (Essential Arts of the Common People), a 6th-century agricultural treatise, was compiled between 533 and 544 by *Jia Sixie* 贾思勰 who was a local official in the North (Jia and Shi 2009). The Essential Arts of the Common People summarized a vast amount of agricultural knowledge that Jia had gained both from previously published texts and personal observations (Knechtges 1997). There is a description of how to make *Hu-bing*

胡 饼 in this book, as an example:

Flour 1 *dou* (10 liters)

Lamb 2 *jins* (1 kg)

Fistular onion stalk 1 *he* (0.1 liter)

Soybean sauce

Salt

"Boil the lamb and fistular onion stalk with soybean sauce and salt together in water until they are cooked. Then put them into the dough and bake it." Although the book has no description of the baking oven, it is tempting to think that this was a type of tandoor (Wang and others 2005).

The raw materials of bakery products in China are simple and low-priced. However, the manufacturing operation can be complicated and sophisticated. The technique that is primarily used is contact baking. Contact baking is a very common type of baking which is widely used, for example for baking of crisp bread, tortillas, pizzas, chapati, pancakes, and pita breads (Feyissa and others 2011). Basically, the dough is placed on hot surfaces (usually iron or ceramic surfaces) heated by coal, charcoal or wood chips.

Two common pieces of equipment used for baking are the stove/oven, and the griddle (*ao-zi*).

A traditional Chinese oven is a semi-enclosed cylindrical furnace. Initially, firewood or coal is burned at the bottom of the furnace to elevate the temperature of the furnace wall to a certain value before baking. After that, the processed pieces of dough are slapped onto the furnace wall one next to another. Because of the high temperature of the contact surface and the hot air within the furnace, the dough becomes cooked. This kind of oven is usually used for the baking of thick dough such as Nang and Shaobing (see Figure 39.2). Specifically, the equipment used to make Nang, known as a "Nang pit", is unique. It is made in many different styles and sizes according to the practical needs.

Figure 39.2 Sesame seed cakes (*Shaobing*) are baked on the inner walls of a heated metal barrel. The high temperature of the heat-conducting wall and hot air cook both sides of the cake, while charcoal is burning in the bottom.

(Courtesy of Ying Ju).

A griddle is a circular flat plate with a somewhat protruding center, three short legs (about 6 cm long), and which is made of cast iron. The modern griddle evolved from the ancient ones made from stone. This equipment got its name "*ao-zi* 鏊子" in Chinese from its turtle-like shape. Underneath the traditional griddle, firewood or coal is burned to heat the griddle surface. In contrast, the heat source of contemporary griddles can be electromagnetic energy, fuel gas, or charcoal. When the surface is hot enough, batter (a non-Newtonian fluid) is poured from a ladle onto the flat surface and then is pressed down with a *pa-zi* 耙子 (a thin plate made of bamboo or wood). In the final step, the cooked pancake is removed from the griddle with a cooking shovel.

Another type of preparation equipment is used to make eggettes and consists of a honeycomb-shaped metal mold (see Figure 39.3). An eggette is a kind of spherical pancake or ball waffle popular in the Cantonese-speaking regions of China, including Hong Kong and Macau. The thin batter, which is made from mixing egg, sugar, flour, and light evaporated milk, is poured into the mold and then placed on the fire to 'roast'. Finally, the baked eggettes are poured out of the mold (or dug out of the mold). The fresh, aromatic flavors of eggettes, sold from street stalls, can be smelled from a long way off.

Figure 39.3 One example of the moulds used to make eggettes. The paste, which is made with egg, sugar, flour and evaporated milk, is injected into the molds.

(Courtesy of Ludan Ye).

Steaming

Mantou 馒头, or steamed bread, is a unique staple food of China, which enjoys a high reputation and is known as the "oriental gourmet". Good steamed bread is neither dry nor stringy, nor will it stick to the teeth. This is mainly because during preparation it is rolled over and over again with some additions of fresh flour. A properly made steamed bread of the right consistency (texture) will hold together, and tastes sweeter the longer it remains in the mouth (Sinorama 1984).

There are a variety of steamed bakery products including Mantou. The characteristics of these are listed as follows:

1. The main material is wheat flour, and the processed dough has dough strength.
2. The dough is fermented using yeast as the leavening agent.
3. Products are cooked using the steaming method.
4. The inner structure of the final products is polyporous with a soft mouthfeel, and flavors of grain itself and the fermentation products.
5. The surface color of the cooked products is close to the color of wheat flour which is ivory.
6. Solid convenience foods such as these have a better taste when they are hot (Peng and others 2011).

Principles of steaming, and equipment

Steaming is an ancient method of cooking in China, and is considered as a healthy cooking technique resulting in better nutrition retention. Steaming utilizes continuously boiling water to produce steam which transfers heat to the nearby food thus cooking the food. A typical steamer is shown in Figure 39.4 and comprises a series of stacked circular containers made of metal or bamboo; such steamers appeared around the time of the Song Dynasty (960–1279). The steamer has a lid that is placed on top of the containers during cooking to allow the steam to cook the food efficiently. For millennia, Chinese chefs have used steaming and boiling as the main methods for cooking vegetables (Coe 2009).

Figure 39.4 Steamer in a roadside breakfast store. This type of steamer is very common in China and is used to steam *Mantou, Baozi*, and various pastries.

(Courtesy of Ying Ju).

Some typical bakery products

Bing

Bing 饼▪, or Chinese pancakes, was one of the earliest forms of pastry. The earliest method of making Bing was to ground the grain to powdered form, make into dough by adding water, then boil in water until cooked. However, over the years other types of pancakes have been developed including those that are steamed, baked, toasted, or fried. As a result, Bing has the most varieties among all dough-based foods. It comes in all sizes and thicknesses, some with stuffing, and even the stuffing comes in no less than several dozen varieties. The non-stuffed pancakes can be single or multi-layered; Chefs with good skills can make around a dozen layers in a pancake, with each layer being as thin as paper (Liu 2004).

Sesame seed cake (Shao-bing 烧饼)

Sesame seed cake is the most popular baked pastry, and can be found in both North and South China. Historically, Chinese people show special preference for Shao-bing regardless of the region where they live and their age (Yu 2007). A crispy Shao-bing, fried *yu t'iao* 油条, a bowl of hearty bean curd milk, and an egg is the traditional favorite breakfast of the Chinese. Shao-bing, also known as "*Hu-bing*胡饼" and "*Chui-bing* 炊饼" in the Tang dynasty (618–907), was introduced to China by the Persians. It was regarded as the ideal food for nomadic people, since it could be easily carried and would keep for a long time (Sinorama 1984). Chinese street vendors have applied their skills and trade for 1000 years (see Figure 39.5). In many areas one may get better food from small food stalls and peddlers than from restaurants (Halvorsen 1996).

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

Figure 39.5 A simple process of *Shao-bing* making is: flatten the dough (a) → brush the top with water (b) → coat the dough with sesame (c) → unroll the dough (d) → place the flat dough on the furnace wall (e and f) → take the cooked *Shao-bing* out of the furnace (g and h).

(Courtesy of Ying Ju).

Jianbing Guozi 煎饼果子

About 100 years ago, pancake was introduced from Shangdong to Tianjin. Today, derivatives of pancake made in Tianjin include *Jianbing Guozi* and *Guoba* dishes 锅巴菜. The former is a uniquely flavored snack in Tianjin. The unfermented batter used to make Jianbing Guozi consists of mung beans, millet, dried small shrimps, condiments, and water. After the batter is made into the pancake, an egg is cracked on top; then the thin pancake is rolled over with sauce and chopped green onion to form a "*Guozi*" which literally means deep-fried dough stick, also called *yu t'iao* in Northern China. Thus, a delicate Jianbing Guozi is made (Yu 2007; Jia 2011).

Kompyang 光饼

Kompyang originates from Fuzhou, the capital city of China's Fujian Province. Kompyang (see Figure 39.6), called *Guang-bing* 光饼 in Chinese, is a kind of cake with a small hole in the center so that they can be strung together to make them convenient to carry. According to legend, Kompyang was named after its inventor Qi Ji-guang. Kompyang is made with flour, salt, soda, lard, and water. The dough is stuffed with other ingredients such as meat, and flattened with a rolling pin. Then a hole is punched in the middle of the round dough using the pommel of a hammer. Finally, it is slapped onto the furnace wall of a traditional Chinese oven and baked for approximately 15 min. Kompyang is not eaten alone as a snack. It is usually cut into two pieces and eaten with a slice of cooked meat or fried beans in the middle. In addition, it can also be boiled or cooked to make soup and other dishes (Cao and Yu 1986; Lin 1987).

Figure 39.6 Kompyang stuffed with meat and other ingredients. A small hole can be seen in the center.

(Photo by Lu Zhang).

Guokui 锅盔

This kind of pancake is baked in a charcoal fire after fermenting the flour, and has a long history as a traditional wheat-based food in China. Similarly to, for example, hamburgers in western countries, it is also a kind of convenient cheap fast food to appease one's hunger, but it does not always appeal to refined tastes. Shanxi Province and Gansu Province are said to be the cradle of the Guokui. Guokui are made using completely traditional methods there, except that the soil pit is replaced by an earthen oven that is half as tall as an average Chinese adult (sometimes discarded oil drums, lined with heat-resistant earth, are used as ovens).

The ovens are filled with charcoal pieces to create a gentle fire, and dough pressed with wooden sticks is baked in a short time. Guokuis made by this method combine the taste of flour with the scent of wood (and it is definitely a joy to have a bowl of mutton soup to go with it). There are also Guokuis made with flat iron pans, which require simpler tools and less time (Yue 2001; Yu 2007).

Nang 馕

The word "Nang" is from the Persian, originally means bread (see Figure 39.7 and Figure 39.8). Nang is popular in Arabia, Turkey, Middle and West Asia. In China's Xinjiang province, Nang is a loved staple food which has a history of over 2000 years. "I can eat no dish for one day, but I can't live without Nang" is a saying of Xinjiang's Uighurs people. Obviously, as a staple food, Nang plays an important role in their daily life, and in fact for Uighurs, *Nang* is sacred (Shan 2005). There are about 50 kinds of Nang and some common varieties are Nang meat, oil Nang, *Wo-wo Nang*, and sesame Nang. Nang has a long storage time due to its low water content, and oil Nang especially can be kept for a few months. Even if it dries out, it becomes soft upon rehydration, which makes it easy to eat. The dough is made of flour mixed with a little saline water and leavened dough. After stirring and proofing, the dough is baked in a special utensil called a "Nang pit" (*Nang-keng* 馕坑 in Chinese) (Yu 2007). A Nang pit forms a central part of Uyghur's long dietetically cultural heritage and is mainly used during the preparation of Uyghur's breads, and for the baking of a wide variety of other foods (Ablat and others 2012).

Figure 39.7 Fresh baked *Nang* exhibits aromas of milk and sesame seeds.

(Photo by Lu Zhang).

Figure 39.8 The underside of a Nang, which has been in direct contact with the furnace wall, is baked and browned with the decorative pattern on it clearly visible.

(Photo by Lu Zhang).

Most well-known pastries

Moon cake

Second to the Spring Festival in importance and grandness is the Mid-autumn Festival, when people get together to enjoy the Moon cakes. Like eating *Zong-zi* 粽子during the Dragon Boat Festival, or having *Tangyuan* 汤圆 at the Lantern Festival, having Moon cakes at the Mid-autumn Festival is a global Chinese tradition. Because of its round shape, like that of the moon, the Moon cake symbolizes the union of a family. Moon cakes and Zong-zi are considered as both desserts and main meals. Even so, Moon cakes come in many flavors. A

traditional variation is where the pastry is filled with lotus seed paste, sometimes with one or two intact cooked/salted egg yolks in the centre. Modern variations utilize novel differences in both the pastry crust and the filling to create even more varieties (Simonds 2005). For example, there are over a dozen kinds of fillings including nuts, lotus seed paste, egg yolk, bean paste, crystal sugar, sesame seed, ham, and more. Also Moon cakes can have different tastes including sweet, salty, salty and sweet, numbingly-hot, and so on. Traditional Beijing-style Moon cakes are made similarly to sesame seed cake, where the outer crust is crispy and delicious. The Suzhou-style Moon cakes also have a crispy outer crust, and consist of many thin layers which are soft and light and pleasing to the tongue. The inner filling of a Cantonese-style Moon cake is the most famous and its crust is similar to that of Western cakes. In addition to the variety of Moon cakes, the modern packaging of Moon cakes is becoming more and more refined and fancy (Liu 2004).

Other pastries

Chinese pastries have a long history, and sophisticated processing technology has been used to develop a wide variety of pastries. According to incomplete statistics, there are hundreds of kinds of pastries in China (Li 2002). For instance, a pineapple tart is a round or rectangular block-shaped short-crust pastry filled with pineapple jam (Simonds 2005; Dou 2010). Vegetarian cakes or pies are currently popular products that often consist of fruit, meat, or vegetables (see Figure 39.9 and Figure 39.10). With the more accelerated pace of modern life, people tend to buy ready-made pastries from the grocery shops rather than making them in their own home.

Figure 39.9 Pineapple tarts. There are different kinds of fruit fillings such as strawberry, apple, and orange.

Figure 39.10 Vegetarian cakes or pies are similar to tarts, but with more crispy crusts.

Other bakery products

Steamed bun

The word Mantou is documented in a poem by the Western Jin Dynasty scholar *Shu Xi* 束皙 (about 264–304), which is appropriately entitled "Rhapsody on Pasta" ("*Bing fu* 饼赋"). He tells us that this is an excellent food to serve at banquets held in early spring (Knechtges 1997):

> At the beginning of the three spring months,
>
> When yin and yang begin to converge,
>
> And the chilly air has dispersed,
>
> When it is warm but not sweltering,
>
> At this time,
>
> For feasts and banquets it is best to serve Mantou.

Steamed stuffed bun

Beijing's neighbor, Tianjin, is a famous port city and its cuisines are also typical of the Northern China style. Its most famous food, the Dog-Won't-Eat stuffed meat buns, has the characteristics of thick-tasting brine (extract), and has symmetrical wrinkles on the bun as a result of kneading the dough to seal in the stuffing; each bun should not have less than 15 wrinkles (Liu 2004).

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40

Italian Bakery Products

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Overview

"White art" (*arte bianca*) is the general term used in Italy to describe the activities that transform wheat flour into a leavened baked product. This definition embodies the fascinating aspects and complexity of this sector. The adjective "white" is immediately identified with flour, an ingredient that plays a key role not only in the production of bread but in all baked products. At the same time, the adjective arouses an impression of lightness and softness, properties that are associated with most of the products in this category, thanks to their alveolar structure.

Creating baked products is a form of "art", since the technological process cannot be considered simply as a sequence of operations applied at set conditions. Wheat flour is the prime raw material for these foods, and each technological phase must be performed to exploit each kind of flour to the utmost according to its characteristics. This applies to many Italian baked products whose formulation includes not only the use of wheat flour but also other sources of starch. In the past, the choice was linked to the greater adaptability of some cereals and non-cereals, with respect to common wheat, to the particular pedoclimatic and agronomic conditions of many areas of Italy.

Such differentiated activities resulted in hundreds of types of bread (INSOR 2000; Bordo and Surrasca 2002) and sweet and savory baked products (Bordo and Surrasca 2003) that differ not only in size, shape, and ingredients, but also for their consumption opportunities. In Italy, "white art" is practiced both at an industrial level and in artisan bakeries which produce highly diversified, high quality products, albeit in limited quantities.

In spite of the complex nature of this sector, it is possible to identify a common matrix in all baked products. In fact, the basic ingredients are represented by cereal flours (usually wheat flour), water, and a leavening agent. Furthermore, although the technological conditions may differ, the process itself includes a number of fundamental operations such as mixing, kneading, leavening, and baking. These phases are necessary for obtaining an attractive and digestible food characterized, at a microscopic level, by a friable crust and an internal alveolar structure. The microscopic structure shows gluten, a reticulated texture that contains swollen, gelatinized starch granules. The protein network is more or less regular and continuous according to the characteristics of the flour, the presence of gluten-free flours in the formulation (both from cereal and non-cereal origins) or of other ingredients (sugar, fats, fibers, and so on) that can interfere with the formation of the gluten structure. The special characteristics of baked goods, as clearly identified by the adjective "baked", are obtained by baking in the oven, a strategic phase not only for the control of the quantity of water that remains in the finished product – which constitutes a critical parameter for its preservation – but also for its nutritional value, structure, and flavor.

Baked products can be classified according to various criteria, the simplest and the most commonly used are shown in Figure 40.1. Products are distinguished using two different parameters: the percentage of sugar in the formulation (sweet or savory baked products) and their texture properties (lightness/softness versus crispness/friability) (Lucisano and Pagani 1997). An amount of sugar equal to 10% of the weight of the flour is easily recognized at a sensory level; conventionally, this value represents the minimum threshold for a product to be classified as "sweet". Examples of this category of products are the typical Italian festivity

cakes like Panettone, Pandoro, and Colomba, and all kinds of biscuits. The different types of bread which do not require the addition of sugar can be considered, in contrast, as the more common "savory baked products". The other two parameters taken into consideration are lightness/softness or crispness/friability characteristics that are related to the specific volume and moisture content of the final product. These textural properties are the result of complex phenomena that occur throughout all the operations of the technological process, from mixing and kneading to baking, through to storage. A product is said to be "light" or "soft" if its specific volume is higher than 2.5–3 mL/g and the moisture is higher than 15%. Lower values both for the specific volume and the moisture give crispness characteristics to the final products.
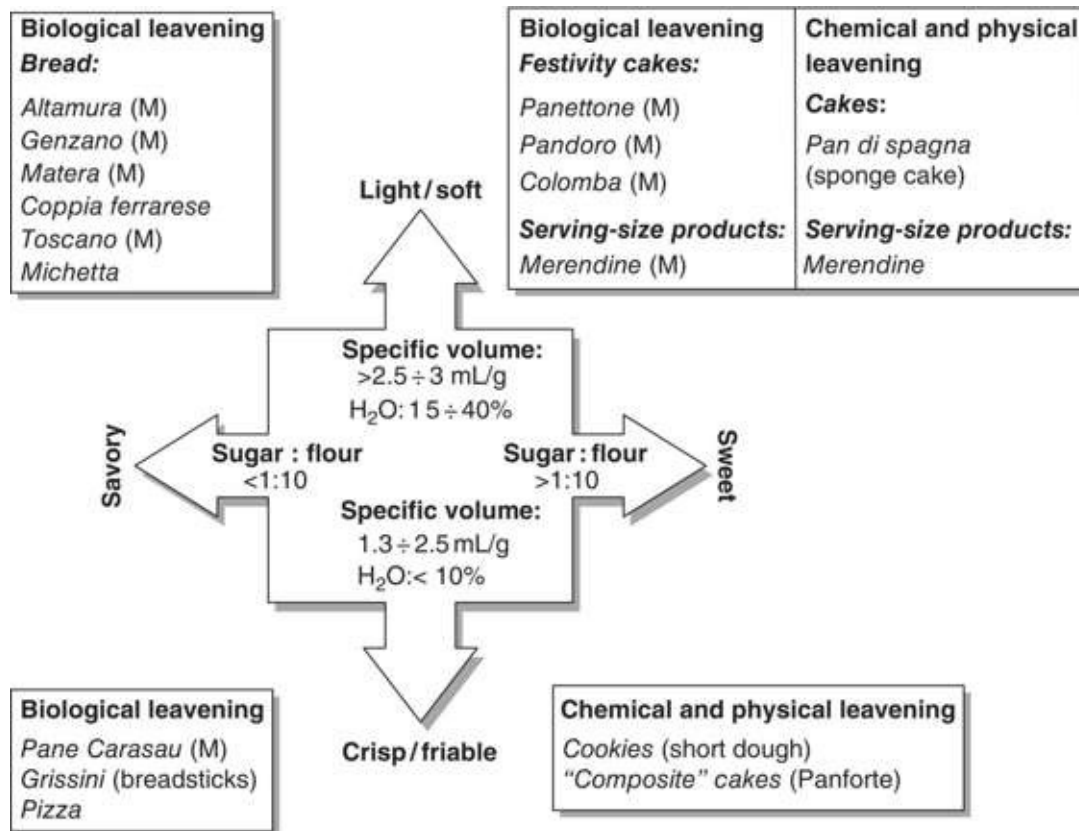
Figure 40.1 Classification of traditional Italian bakery products on the basis of specific volume and formulation (M = *madre* (mother dough), products obtained with sourdough).

In applying these criteria to Italian baked products, we can identify four categories of baked goods that can be further distinguished according to the methods used for the leavening phase. Leavening methods can be distinguished as biological fermentation and chemical and/or physical leavening. Both sweet and savory products made with the sourdough process are of special significance in Italy. For thousands of years, only the sourdough process was used until the discovery of baker's yeast in the 19th century, and it is still widely used in traditional products as this is the best method to guarantee a well-defined fragrance. This process is applied to the products listed in Figure 40.1 and marked with the letter M, from *Madre*, the Italian expression that indicates the "mother-dough" – also called seed sour or sourdough starter – on which this technology is based.

The names and the traditional production areas of the most interesting, well-known, and appreciated products both in Italy and abroad are given in Figure 40.2 and a detailed description of some of these products is provided here, classifying them into two categories: savory (bread and similar products) and sweet.
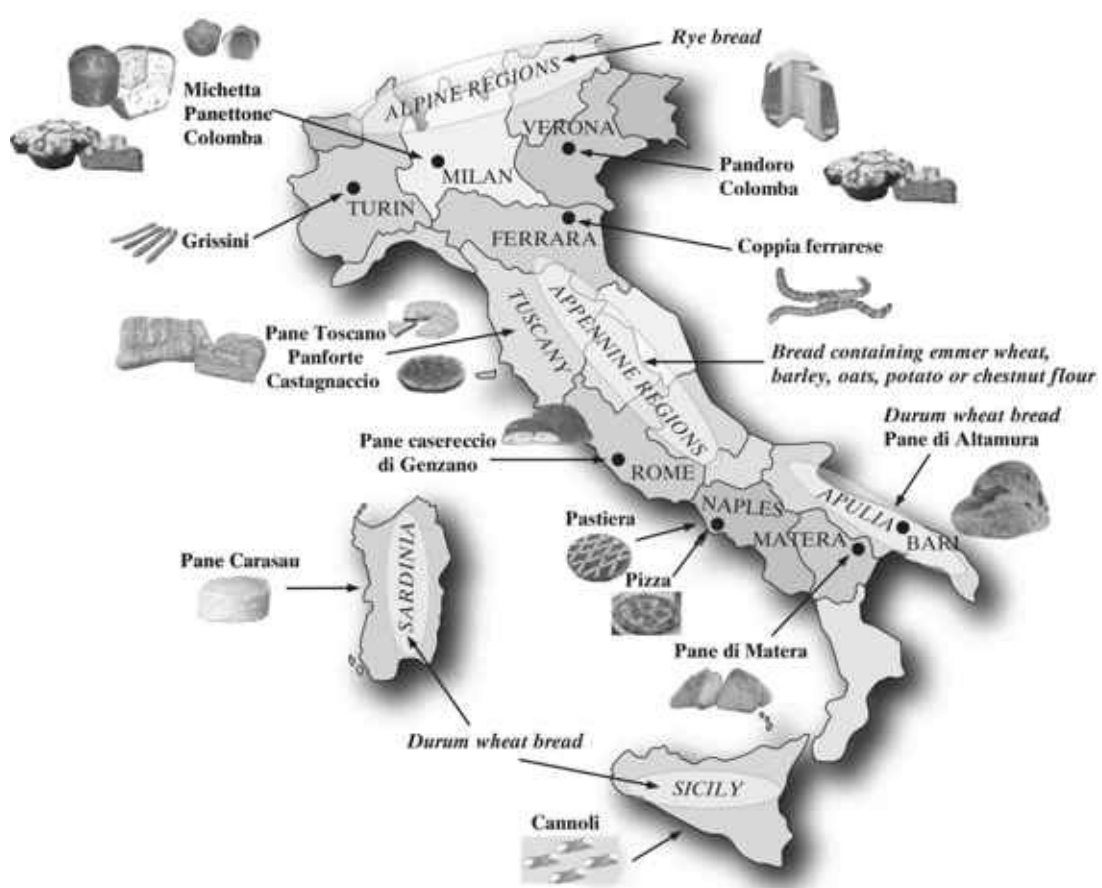
Figure 40.2 Traditional production areas of the most well-known Italian bakery products.

Italian bread and similar products

The hundreds of types of breads available in Italy have interesting common characteristics which make them immediately recognizable on the international market. Some of the distinguishing features are listed in Table 40.1. A peculiar characteristic is the absence of a pan used in the leavening and baking phases, thus enhancing the possibility of forming the bread into endless numbers of shapes and sizes. Furthermore, the widespread use of sponge and dough or sourdough processes, associated with low productivity and with the limited shelf-life of the product, partly justifies the widespread presence of artisan bakeries throughout Italy. In fact, artisan bakeries still constitute the majority of the bread-producers and are present throughout the country.

Table 40.1 Common and peculiar features of bread making for typical Italian breads

Production step	Features
Formulation	No sugar addition
Bread making process	Preference of sponge and dough or sourdough process No pan utilization for the dough leavening and baking Direct contact of the leavened dough with the oven surface

Final product characteristics	Crust with high friability
	
	Uneven crumb grain
	
	No packaging material
	
	Shelf-life
	
	    rolls (50–200 g): max 1 day
	
	    large loaves (500–2000 g): max 1 week

As stated by Dobraszczyk and others (2001), bread making can be considered as a series of aeration stages of a hydrated mass formed by a mixture of protein fibrils with adhering starch granules. In fact, the gas trapped during kneading provides the nuclei for the subsequent gas expansion when the dough is leavened (Delcour and Hoseney 2010). Therefore, development in volume, the ratio between volume and weight (specific volume), and the size distribution of the alveoli represent the physical characteristics that are universally used for defining the quality of bread (Pyler 1988; Crowley and others 2002). At the macroscopic level, these indices show how the crumb alveolar structure (percentage of alveoli with respect to total volume, distribution of coarse and fine alveoli, and so on) is formed and, together with moisture, represent the complex result of the interaction between the properties of the raw material and the conditions applied at each phase of the bread making process. A rapid and accurate procedure for the evaluation of the crumb structure is represented by Image Analyses (Crowley and others 2000; Riva and Liviero 2000; Mariotti and others 2006). A summary of the variability found for each of the above indices for a number of the most representative types of traditional Italian breads is provided in Table 40.2. For many types of Italian bread, the presence of large alveoli in the crumb is not considered a defect, in contrast with the common and widespread statement that an irregular cell distribution is undesirable

(Cauvain and others 1999).

Table 40.2 Physical characteristics of some typical breads[a]

Bread	Raw material (flour)	Leavening process	Moisture (%)	Weight (g)	Specific volume (mL/g)	Porosity[b] (%)	Large cell area[c](%)
Soft							
Pane di Altamura	Durum wheat	M	40–45	500–1500	3.2–3.7	35–40	30–35
Pane di Genzano	Common wheat	M	30–35	2400–2600	2.5–3.0	20–25	32–38
Pane di Lariano	Common wheat	M	33–38	2700–2900	2.5–3.0	30–35	20–25
Coppia Ferrarese	Common wheat	S&D	9–10	200–300	4.0–5.0	28–33	55–60
Pane Toscano	Common wheat	M	38–42	500–1600	3.3–3.7	25–30	15–20
Michetta	Common wheat	S&D	20–25	50–60	10.0–15.0	75–80	90–95
Pasta dura	Common wheat	S&D	25–27	56–60	2.8–3.2	10–15	25–30
Ciabatta	Common wheat	S&D	27–32	150–400	4.0–7.0	27–33	60–70
Pane di segale	Rye	M	40–45	200–250	1.8–2.1	15–18	10–20
Pane al mais	Common wheat and corn	S&D	35–40	250–450	3.5–4.0	25–30	0–5
Crisp							
Pane Carasau[d]	Durum wheat	M	6–8	50–55	2.0–2.2	Absent	Absent
Grissini	Common wheat	M; S&D	5–10	15–25	3.8–4.8	25–30	0–25

[a]Unpublished data.

[b]Cell area/total area.

[c]Cell with area higher than 25 mm^2/total area.

[d]Two baking steps in bread making process.

M, Mother (sourdough); S&D, sponge and dough.

Raw materials: wheat flour and other cereal flours

Common wheat (*Triticum aestivum* L.) flour is universally considered the prime raw material for bread production because of the presence of gluten-forming proteins that assure a viscoelastic dough, which is indispensable for transforming a compact mass into an alveolar structure (Delcour and Hoseney 2010).

Flour suitability for use in bread making is best described by the behavior of the dough produced under standard conditions and assessed using the most common instruments of descriptive empirical rheology such as the Brabender Farinograph and the Chopin Alveograph. Nowadays, other imitative tests have been proposed to determine the quality and the processing characteristics of flour and dough such as the Perten micro-doughLAB, which operates with a small amount of sample, or the Chopin Mixolab, capable of imitating dough performance during kneading and baking because it measures dough performances as a function not only of mixing and time, but also of temperature. To obtain a good yield and bread with high specific volume, the flour must be characterized by a high level of gliadin and glutenin of good quality, high water absorption capacity, long stability times during mixing and kneading (assessed by the Farinograph test), high strength values ($W > 220 \times 10^{-4}$ J), and a good balance between dough strength and extensibility (expressed by the Alveograph index P/L between 0.4 and 0.6).

The availability of common wheat and consequently of flour in Italy is, nevertheless, distinctly lower than the quantity used, especially those wheat varieties with high bread making qualities. For the past few years, Italian production of common wheat has been decreasing significantly: from 3.3 million tons in 2005 to 2.8 million tons in 2010, while imports of common wheat, indispensable for satisfying the needs of the bakeries, have well exceeded 4.5 million tons, representing 60% of the internal demand (ANACER 2011). Although this situation is partly linked to European Union policies and to unfavorable pedoclimatic conditions, one should not forget the scant "vocation" for the cultivation of this cereal in Italy. Because of the specific configuration of Italy, a narrow peninsula approximately 1200 km long where 41% of the area is hills and 35% is mountains, the cultivation of common wheat is mainly limited to the plains of the northern regions (83% of the total production), where it is in competition with corn, a cereal with consistently higher productivity. The pedoclimatic characteristics of the Alpine and Apennine regions, where intensive farming is not possible, have given rise to the development of other crops that have fairly good productivity and are therefore economically profitable. This explains the significant diversification of the raw materials used for bread making in Italy, a tradition that has recently found renewed interest with both consumers and the scientific community. In particular, the resistance of rye to the harsh winter temperatures of the Alps and its greater availability in this area justifies the many types of rye-based breads produced throughout the centuries in the entire Alpine area and which are still produced and consumed (INSOR 2000). Sourdough leavening is also preferred, given the low bread making quality of rye, in accordance with the traditions of the central and north European countries where this cereal is widely used for bread making (Salovaara and Autio 2001; Stolz 2003). On the other hand, breads containing emmer wheat (*Triticum spelta*), barley, potato, and chestnut flours are still common in central Italy (Bordo and Surrasca 2002), an area with a milder climate but with a soil that is not suitable for intensive farming. Agronomic conditions in southern Italy (Puglia in particular) and in the two main islands Sicily and Sardinia, where durum wheat (*Triticum durum* Desf.) has been cultivated for thousands of years with excellent results in both quantity and quality, are completely different. The most frequent types of breads produced,

consumed, and appreciated in these areas contain remilled semolina of durum wheat and are made using the sourdough process, a technology that achieves better results with this particular raw material (INSOR 2000; Consorzio Gian Pietro Ballatore 2001; Bordo and Surrasca 2002).

Using flours other than common wheat in bread making promotes dough systems with special rheological properties and technological performance. Raw materials such as rye, whose proteins have a lower capacity than wheat proteins to produce a viscoelastic gluten network, provide mixtures with low farinographic stability, low expansion capacity when subjected to the Alveograph test, and a high stickiness. The low bread making quality can be improved only with the addition of significant percentages (60–80%) of wheat flour with superior gluten performance. The bread making performance of wheat mixtures enriched with gluten-free flours, such as composite flours both of cereal and non-cereal origin (Mariotti and others 2012), results in a critical "dilution" of gluten that has a negative influence on regular network formation and consequently on the development of product volume (Zhang and others 1998; Dendy 2001).

The rheological properties of the dough obtained with durum wheat semolina are completely different. They are distinguished by a high resistance to deformation and consequently limited extensibility – typical characteristics for the proteins of this raw material (Boyaciogly and D'Appolonia, 1994; Pogna and others 1996) – which allow only a modest development in mass volume during leavening. To be judged suitable for bread making, the semolina must have a high protein content, a good farinographic stability, and alveographic P/L index values below 1 (Boggini and others 1995, 1997). This is confirmed by studies on the characterization of semolina used for the production of *pane di Altamura* (see the process card), the most famous Italian durum wheat bread (Pasqualone and others 2002; Raffo and others 2003). The same works state that the quantity and quality of the protein component of the raw material are important not only for the properties of the dough but also for their influence on the hydration phenomena during the bread making process and the water loss rate from the crumb during bread storage, all phenomena that greatly influence the shelf-life of bread.

Formulation

With regard to product formulation, the quantity of water added to the flour has a significant effect on the rheological properties of the dough and consequently on the bread crumb alveolar structure. Low humidity doughs (about 35–40% water) are firm and stiff; during the leavening phases, their expansion is considerably limited, giving bread with a compact and dry crumb texture, like in *pane di pasta dura*, a type of bread more resistant to mold due to its low moisture content. High humidity doughs (65–70% water), however, cannot be molded into regular shapes and the CO_2 developed during leavening tends to collect into large bubbles forming irregular, flat loaves called *ciabatta* with uneven grain (see Table 40.2 and Figure 40.3).

(a)

"U sckuanète"
("folded" bread)

"U cuappidde de prèvete"
("priest's hat" bread)

"U puène muèdde"
("farmer's" bread")

13 cm

(b)

15 cm

(c)

10 cm

(d)
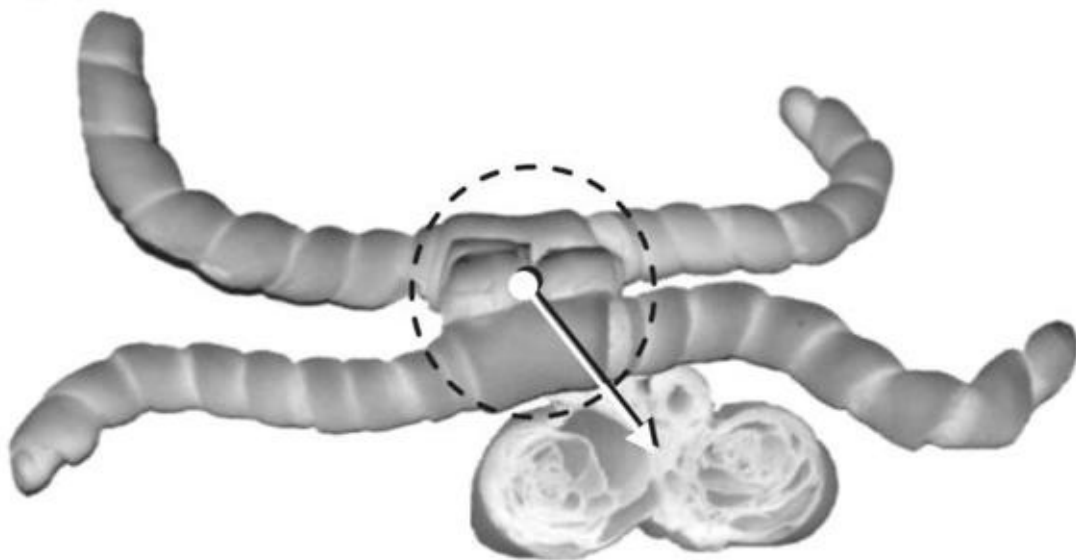
10 cm

(e)
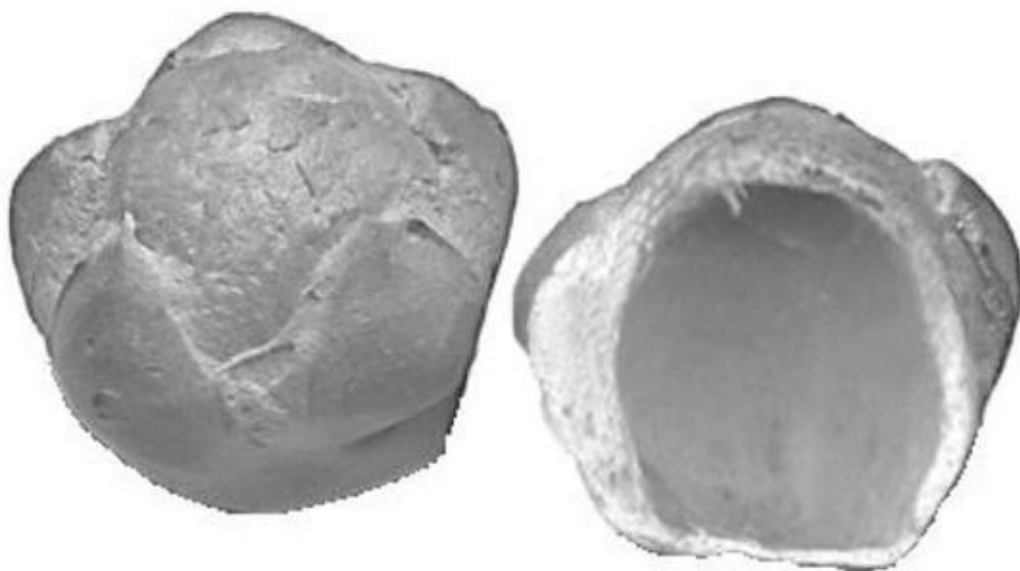
4 cm

(f)

Ciabatta
("slipper" bread)

5.5 cm
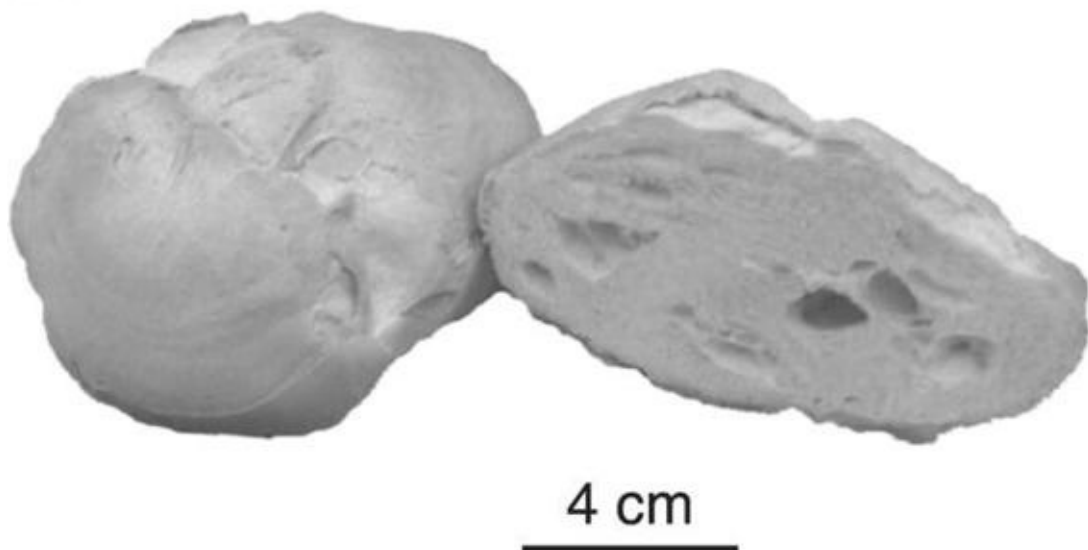
Figure 40.3 Shape and crumb grain of some typical Italian breads: different loaf shapes of pane di Altamura – the traditional names are given in the Puglia dialect (a); the PDO mark is represented in the upper left corner; pane casareccio di Genzano (b); pane Toscano (c); coppia Ferrarese (d); michetta (e); ciabatta (f); pasta dura (g) (see also Table 40.2 for other physical characteristics).

Moreover, the simplicity of Italian bread recipes has to be highlighted. Usually the recipe requires the addition of water and baker's yeast to the flour and does not include significant quantities of sugar or other high hydrophilic substances that are widely added in other countries to maintain the crumb softness for extended periods. Consequently, many types of bread, especially smaller rolls (less than 200 g), generally have a limited shelf-life of no longer than 24 h due to their relevant increase in consistency. The rapid ageing of these products is no doubt influenced by the fact that in Italy most bread is sold as an unpackaged product (ISMEA 2002).

Leavening processes

The different phases of bread making are reported and the specific objectives and effects of each technological step are summarized in Table 40.3 (Pagani and others 2007). The production of bread in Italy is traditionally a discontinuous process, since each phase of kneading, leavening, and baking is performed on a limited amount of material with a separate machine for each technological step. The discontinuous bread making processes are performed using the straight-dough (in Italian *metodo diretto*) or the sponge and dough (*metodo indiretto*) processes; the sourdough bread process can be considered as a particular sponge and dough method (Figure 40.4).

Table 40.3 Characteristics of lactic acid bacteria and yeasts isolated from sourdough of Italian typical baked products

Source: from Italian references cited in section Sourdough process

Genus	Species	Fermentation	FQ[a]	Optimal temperature °C (°F)	Recovery rate

Lactic acid bacteria

Genus	Species				
Lactobacillus	*acidophilus*	Obligate homofermentative	>20	37–42 (98–108)	Low
	amylophilus				Low
	amylovorus				Low
	delbrueckii				Low
	farciminis				Medium
Lactobacillus	*alimentarius*	Facultative heterofermentative	10–20	30–35 (86–95)	Low
	casei				Medium
	curvatus				Low
	paracasei				
	plantarum				High
Lactobacillus	*brevis*	Obligate heterofermentative	1–5	25–30 (77–86)	High
	buchneri				Medium
	fermentum				High
	fructivorans				High
	hilgardii				Low
	pontis				Medium
	sanfranciscensis				High
Enterococcus	*spp.*	Homofermentative	>20	37–42 (98–108)	Medium
Pediococcus	*spp.*	Homofermentative	>20	25–30 (77–86)	Low
Leuconostoc	*spp.*	Heterofermentative	1–5	20–25 (68–77)	Medium
	citreum				Low
Lactococcus	*lactis*	Homofermentative	10–20	25–30 (77–86)	Low

Yeast

Genus	Species				
Debariomyces	*hansenii*	Alcoholic		25–30 (77–86)	Medium
Hansenula	*anomala*			25–30 (77–86)	Low
	subpelliculosa				Low
Pichia	*guilliermondii*			25–30 (77–86)	Low
	saitoi				High
Saccharomyces	*cerevisiae*			25–30 (77–86)	High
	exiguus			20–25 (68–77)	High
Torulaspora	*delbrueckii*			25–30 (77–86)	Medium
Candida	*holmii*			20–25 (68–77)	High
	krusei				High
	milleri				Medium

	(humilis)			
	robusta			Medium
	stellata			Low
Rhodotorula	*glutinis*		20–25 (68–77)	Low

[a]FQ, Fermentation quotient = lactate/acetate molar ratio.
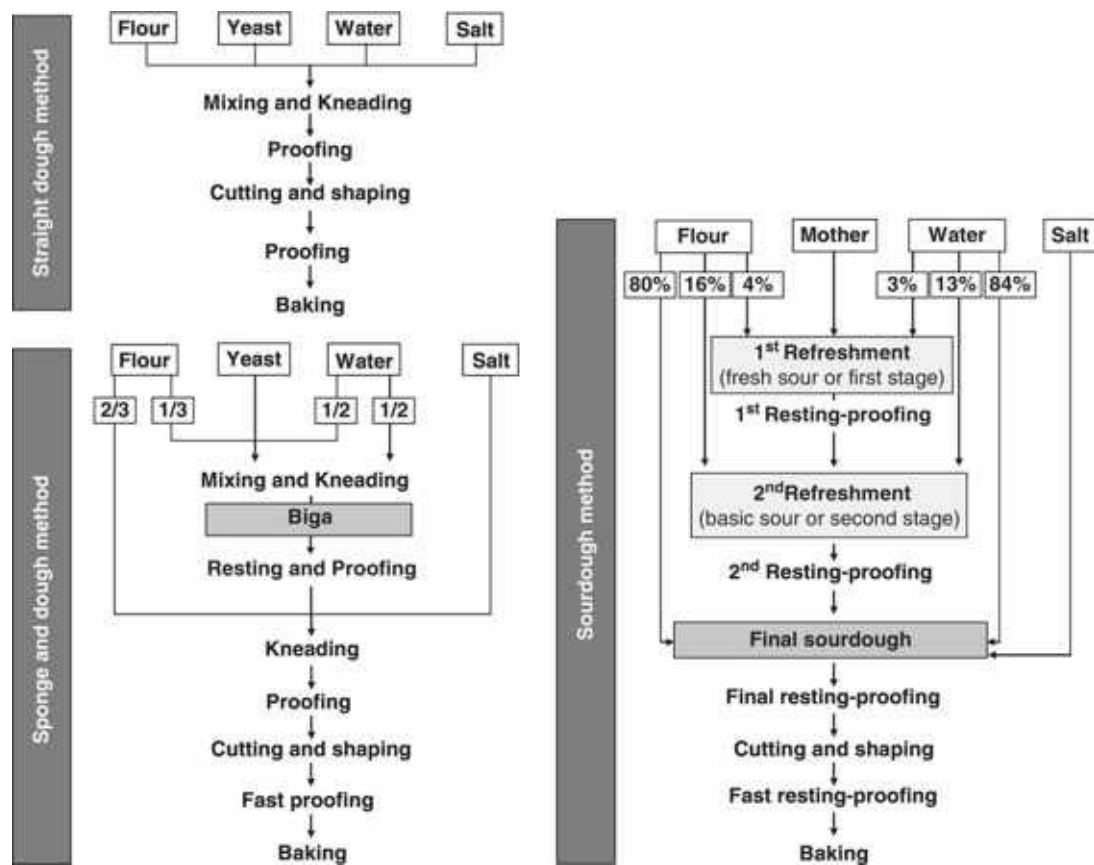
Figure 40.4 Bread making processes.

Straight dough and sponge and dough

With the straight-dough method, all the ingredients are mixed together at the same time to form a dough which is then left to rise. The yeast is made up of selected cultures of *Saccharomyces cerevisiae* and fermentation must occur in at least two phases. The first fermentation, called *puntata*, is generally effected on large masses of dough for variable periods of time, from about 30 min to 3 h, according to the process. The objective of this operation is not to obtain an increase in volume but to induce important changes in the rheological properties of the dough (Chargelegue and others 1994); in particular, the solubilization of part of the CO_2 produced lightly acidifies the system and causes the gluten to become stronger. This phenomenon improves kneading of the dough and its ability to maintain the shape it is given during the second fermentation or *appretto*. In this phase, the dough is left for 1 h under controlled temperature and relative humidity until it has reached its maximum volume. The advantage of using the straight-dough method, thanks to its speed and use of compressed yeast, is the possibility of using lower-strength flours as a lower leavening time is required.

In the sponge and dough processes, the ingredients are added at different times (Figure 40.4). Given the simplicity of the recipe of most Italian breads, the adoption of sponge and dough

processes is one of the methods that has been perfected over the centuries to slow down ageing. There is the formation of a preparatory sponge, called *biga*, which involves mixing part of the compressed yeast (selected *Saccharomyces cerevisiae* strains), part of the flour, and part of the water required for the entire formulation. The sponge is allowed some time to rest (from 3–4 to 20 h according to the type of bread). During the long rest phase, the yeast adapts itself to the dough system, and reaches optimal fermentation capacity when all the ingredients have been added. At the end of this long step the remaining flour and water are added. After 30–60 min of leavening, the dough is cut, shaped, and left to rise again for about 1 h, and is then baked.

The long leavening times required for the sponge process provides, in the final product, a crumb grain texture with a high number of alveoli (Brown 1993), often with an irregular size distribution. This structure provides greater initial softness, as indicated by the lower hardness and longer storage times than for products obtained using the same raw materials and the straight-dough process, which is in agreement with the results of Fessas and Schiraldi (1998), who showed the key role of alveolar crumb structure in the sensory texture of bread.

Sourdough

Even more interesting are the effects on bread characteristics (see Table 40.2) associated with the sourdough process. This procedure takes its name from the sharp acidification that occurs due to the microorganisms present in the dough. The microbial groups are linked in a non-competitive and often mutualistic equilibrium, forming an ecosystem that is quite stable to external perturbation (Martinez-Anaya and others 1990; Foschino and others 1995; Gobbetti 1998; Stolz 2003; Pagani and others 2013). Generally sourdough contains yeasts (about 10^6–10^7 cfu/g) of the *Saccharomyces* and *Candida* species, which are responsible for the alcoholic fermentation and consequently for the development of the volume of the dough. The yeasts are associated with lactic acid bacteria (LAB) of the genera *Lactobacillus, Pediococcus*, and *Leuconostoc* in a ratio yeasts : lactobacilli of 1 : 100 (Ottogalli and others 1996; Stolz 2003). LAB perform an intense acidifying activity producing lactic acid and acetic acid in quantities related to the species present in the sourdough (obligate homofermentative, facultative heterofermentative, and obligate heterofermentative) (Foschino and Galli 1997; Stolz 2003), all capable of determining both a significant increase of the total titratable acidity and a decrease in pH.

These changes not only influence the sensory properties of the dough and the finished product (Schieberle 1996), but also their consistency (Crowley and others 2002), thus providing an extended shelf-life (physical and microbiological) of the bread obtained using this process (Röcken 1996; Corsetti and others 1998; Raffo and others 2002, 2003). The metabolites produced by the amylase activities (sugars and low molecular weight maltooligosaccharides with degree of polymerization from 3 to 9) and the protease activities (peptidesw, amino-acids) performed by the LAB are equally important for assuring fragrance and prolonging shelf-life, as illustrated in a review by Martinez-Anaya (1996) and in the work of Gobbetti and others (1996). Moreover the changes in the hydration state of the gluten proteins promoted by souring could also be involved in keeping the crumb fresh for longer (Crowley and others 2002). Nevertheless the delay in bread staling associated with biological acidification can vary according to the LAB strains and the level of acidity obtained (Corsetti and others 1998, 2000).

The development and maintenance of the microbial species typical to sourdough are achieved using traditional discontinuous processes which require subsequent refreshments of the primary dough (seed sour from a previous batch), to obtain the full sourdough after a single or multistage process (Ottogalli and others 1996; Vogel and others 1996). The production of *Altamura* bread according to its regulation (EC 2003) requires at least three phases. Generally, in traditional Italian bread making processes, the seed sour represents 5–20% (w/w) of the final dough.

The microbial composition of sourdough samples from different bread producers shows considerable variability. Although all producers apply a constant microorganism propagation process in their bread making, the sourdoughs differ both in their formulation and in their storage conditions. These factors are conducive to specific symbioses between microorganisms with interesting repercussions on the sensorial properties of the finished product. The microbial species (both LAB and yeasts) found in the sourdough of regional breads and discussed in several works by Italian authors are summarized in Table 40.3 (Galli and others 1988; Gobbetti and others 1994, 1995a, 1995b; Foschino and others 1995; Corsetti and others 1998, 2001; Pulvirenti and others 2001; Ricciardi and others 2002). There are no substantial differences regarding the microbial species found in the mother dough of rye bread and wheat used in other countries, as highlighted in the review of Stolz (2003) and the studies of Infantes and Tourneur (1991) and Infantes and Schmidt (1992). As emphasized by Gobbetti and Corsetti (1997), in agreement with all researchers engaged on this subject, *Lb. sanfracinscensis* can be considered the key bacterium in the sourdough process. Together with *Lb. pontis*, it makes up the major part of the microbial flora (10^8–10^9 cfu/g) and establishes interesting trophic relationships with the sourdough yeasts (*S. cerevisiae* and *S. exiguus*) due to its effective maltose metabolism (Stolz and others 1993). The overall metabolic activities of these dominating bacteria ensure rapid acidification, a balanced production of lactic and acetic acid (as expressed by the Fermentation Quotient (FQ), that is, lactate/acetate molar ratio), and gas production.

The difficulties involved and the careful handling required when using sourdough to maintain the correct balance between the microorganisms of the sourdough and, at the same time, the improved quality of the bread obtained with this method, explain the considerable interest shown in the development of selected starters that could provide a quality product using a simpler process (Foschino and Galli 1997). This approach, largely used in rye sourdough (Stolz and Böcker 1996; Kulp 2003), has been examined by Catzeddu and others (2002) for the production of good quality *pane Carasau* (the well-known Sardinian crispbread; see the process card): the authors proposed a microbial starter containing some LAB and yeasts isolated from different sourdoughs of this bread.

For some time now, new proposals have been exploited for improving the sourdough process with methods that maintain the advantages associated with acid dough and simplify the management of the technological cycle. Type II sourdough and type III sourdough may be considered interesting examples for these purposes (Pagani and others 2007). Type II sourdough is a semi-fluid and pumpable dough used in continuous processes to ensure correct acidification and, at the same time, to satisfy the requirements of industrial processes for ease of control and working times. These preparations are characterized by long fermentation periods (from 2 to 5 days) and fermentation temperature sometimes higher than 30 °C to speed up the process. As stated by Stolz and Böcker (1996), this approach has

transformed traditional sourdough technology "from work-consuming multiple-stage processes (the type I sourdough) to work-saving one-stage processes", capable of ensuring flexibility and stability in the final product characteristics.

The development of this technology is represented by equipment that provides for continuous sourdough fermentation (Stolz and Böcker 1996; De Vuyst and Neysens 2005). This process has been adopted in Italy by a small number of producers of festivity cakes and breads at the industrial level. In this case, and similarly to what has occurred in other food sectors, the starter, also called pre-ferment, is represented by LAB selected cultures (rarely in combination with yeasts) sold in the form of lyophilized granules. Under these conditions, *Lb. sanfranciscensis* is not sufficiently competitive to dominate the fermentation. The ecosystem is characterized by LAB of other genera and species, both homofermentative and heterofermentative. A thorough and extended revitalization phase of the microorganisms in fermentation reactors for 16–18 h at 27–32 °C is needed, generally in presence of flour. After this period, the liquid pre-ferment is mixed with the remainder of the ingredients and processed according to the particular technology of each product (Stolz and Böcker 1996).

The main steps for the production of lyophilized starters is shown in Figure 40.5. Starting from selected strains (mother culture), an intermediate culture is obtained that is further fermented in a larger size reactor. The biomass is then separated, washed with isotonic solutions, concentrated, and after the addition of cryoprotectants, lyophilized, ground, and packed to obtain a standardized culture.
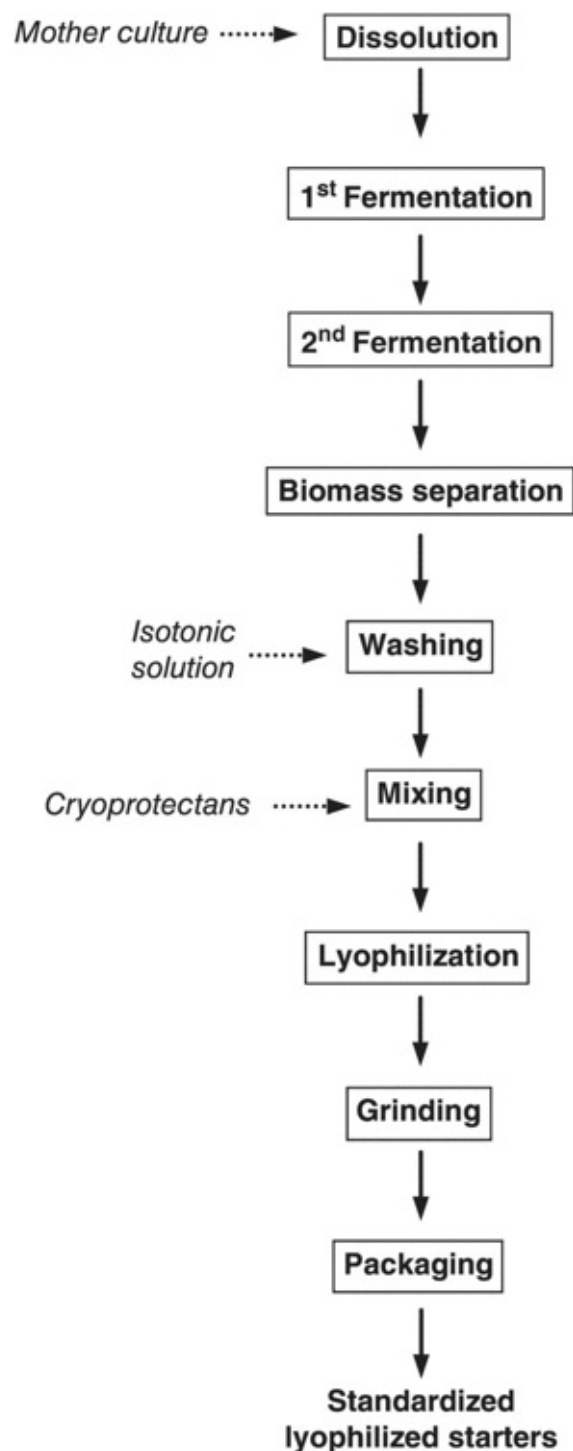
Figure 40.5 Process flow chart for standardized lyophilized starters.

Although the starters have significantly simplified the production of sourdough, this approach is still considered too expensive for small artisan producers because of the need for reactors and long fermentation times (from 16 to 24 h to obtain the full sourdough). These disadvantages may be overcome in part by type III sourdoughs or dried sourdoughs (*madri essiccate* in Italian) containing LAB resistant to the drying process (Hammes and Gänzle, 1998). The acid content of these preparations is extremely important since it determines both the technological characteristics of the product and the fragrance. Other advantages of dried sourdoughs include ease of use and high standardization, a longer shelf-life, and easy storage. Type III sourdoughs are commercial products that are obtained from mature sourdough and stabilized using spray drying or drum drying. The most popular microorganisms for this process are *Lactobacillus* of the *plantarum, brevis, casei, diacetylactis, fermentum* and *Pediococcus acidilactici* and *pentosaceus* species since they have a greater resistance to

drying (Martinez-Anaya 2003). Unlike type I sourdoughs, doughs of types II and III require the addition of baker's yeast (*Saccharomyces cerevisiae*) as a leavening agent.

Baking

As mentioned before, another common characteristic of most types of Italian bread is the baking method (Table 40.1). In fact, in contrast to the Anglo-Saxon tradition, Italian bakeries do not use a pan for the dough rise from the first leavening phase, and this enables them to obtain an almost unlimited number of shapes and sizes, but it also influences the methods that have to be used prior to baking, from the selection of the flour to the final shaping. A good quality flour, skill, and experience are required, since the leavened product can easily lose its shape if the mixing and kneading are not done correctly. In addition, as a pan is not used and the bread is in direct contact with the oven surface, the crust formed is significant (thickness 2–3 mm) in loaves of 1 kg or more. A crust with a high friability (moisture in the crust less than 5–8%) (Calvel 2001) is greatly appreciated by consumers, but it is another element that reduces the product's shelf-life. The high moisture gradient formed between the crust and the crumb when the bread is removed from the oven determines water migration phenomena between the internal more humid part and the external drier part, which are critical to bread storage (Kulp and Ponte 1981). However over the centuries, the imagination and skills of Italian bakers have given rise to the development of ingenious solutions for prolonging shelf-life which are still in use today. There are two methods and both involve the control of product moisture. The first technological method concerns the maintenance of high humidity in the crumb; this ensures softness when chewing and can be easily guaranteed by large loaves (>500 g) and the use of sourdough. Acidification can also cause a different distribution of water between starch and proteins, which is useful for maintaining the softness of the product (Piazza and Masi 1995). Note that acid dough usually contains a greater quantity of the highly hydrophilic compounds, sugars and low molecular weight dextrins (Martinez-Anaya 1996). The second method used to ensure a longer shelf-life reduces the humidity of the product to a level that prevents both microbial changes and the migration of water within the product. One of the most interesting examples is the Sardinian bread *pane Carasau*, which had to have guaranteed stability for several months, for the entire period that the shepherds spent far from home (INSOR 2000; Catzeddu and others 2002). This was obtained by preferring the sourdough bread making processes, with long maturing and fermentation times that ensure the formation of an extremely fine rolled dough, and by perfecting a double-baking process which significantly decreases the humidity of the product to 6–8% (see Table 40.2). Products with an equally long shelf-life have been developed in several regions. Some examples are well known worldwide, such as *grissini* (see the process card), the bread-sticks from the area near Turin, and *taralli*, typical products of the Puglia region (INSOR 2000). For taralli, the final low humidity of the product is assured by its special geometric form which promotes a large evaporation surface.

Oven temperature is a determining process variable for the crumb grain structure of bread. A striking example is the *michetta* (see the process card), a small roll (generally 50 g) typical of the Milan area and northern Italy. If the product is baked in ovens with a maximum temperature of 240–250 °C/464–482 °F (together with plenty of steam in the chamber for approximately half the baking time), the flash-evaporation of the water is promoted with a formation of a large bubble in the center which confines the crumb to the external part of the

product and assures the highest specific volume among the traditional breads (see Table 40.2 and Figure 40.3). In contrast, at lower temperatures (not exceeding 200–220 °C/392–428 °F) the division between the large and small alveoli in the baked bread can be compared to that which distinguishes the dough at the end of the leavening phase.

The "typicalness" of Italian bread

In the past few years European consumers, and in particular Italian consumers, have been rediscovering and appreciating the characteristic foods of their countries as representative of culture and traditions. The wide diversification that exists at the agro-industrial production level in Europe has been recognized and provided for in the EEC Council Regulation No 2081/92 (EC 1992) which has defined two different types of geographical designation of origin for agricultural products and foodstuff.

The Protected Designation of Origin – PDO denomination (*Denominazione di Origine Protetta*, DOP in Italian) is assigned to products that have a strong link with their region of origin. Two conditions must be satisfied to receive the PDO designation: production of the raw materials and their processing through to the finished product must be made within the region. Furthermore, evidence must be provided that the special quality characteristics of the product are exclusively or essentially dependent on the geographical environment (climate, quality of the soil, human factors, and so on) of the place of origin.

Even the Protected Geographical Indication – PGI denomination (*Indicazione Geografica Protetta*, IGP in Italian) expresses a bond between the product and the region. Nevertheless, this dependence is not so strict because it is not essential for all the phases of the transformation process to be performed in a particular geographical area. A PGI product nonetheless complies with the strict production regulations established for the production process and the compliance with these regulations is assured by the inspection body.

On a par with the situation present for years in other market sectors such as the wine, cheese, and cured meat sectors, many breads produced in Italy are characterized by a strong specific regional identity. Some of these products have already obtained the PDO denomination (*pane di Altamura, pagnotta del Dittaino*) or the PGI denomination (*pane casareccio di Genzano, pane di Matera and poppia Ferrar*ese). Recognition of typical products for *pane Toscano* has been initiated. It is important to emphasize that the recent rediscovery of these products by the consumer and the consequent increase in demand have finally channeled research towards a detailed characterization of several types of bread, for both the identification of the properties of the raw materials and the phenomena that occur during some of the phases of the technological process.

Process cards of typical Italian breads

Pane di Altamura

This bread from the Puglia region is obtained from remilled semolina of four durum wheat varieties – Appulo, Arcangelo, Duilio and Simeto – grown in the Altamura area (not far from Bari). These raw materials can be used on their own or in combination, making up at least 80% of the total semolina. The production specifications (see also www.panedialtamura.net) specify all the bread making steps which are described in every detail. The official recipe consists of 20 parts full sourdough to 100 parts durum wheat remilled semolina, 2 parts salt, and 60 parts water. The full sourdough is prepared by adding ingredients at least three times (refreshment steps). The final kneading takes 20 min and the mass is then covered with a thick cloth to maintain a constant temperature and left to rest for 90 min. The final shape is

obtained through three distinct molding phases, each with rest phases (intermediate proof) of established times. The baking operation must also be performed under controlled conditions in ovens heated with oak wood to obtain bread loaves with the characteristic crust of at least 3 mm thick and the typical flavor, due both to the presence of durum wheat semolina and to the sourdough process.

The traditional shape of pane di Altamura resembles a hat with a wide brim (Figure 40.3a). It is also produced as a large loaf which can weigh up to 2 kg. Its main characteristic, as well as the typical yellow color of the crumb caused by semolina pigments, is its long shelf-life of at least one week (Raffo and others 2002, 2003), equal to the time the farmers and shepherds spent with their herds before returning home.

Pagnotta del Dittaino, made using sourdough and remilled semolina obtained from durum wheat grown in the different municipalities near Enna and Catania (Sicily region) has recently gained the PDO denomination (EC 2009a).

Pane casareccio di Genzano

The production area of this typical bread is the town district of Genzano, 30 km from Rome. It was the first Italian cereal product to obtain the PGI denomination from the EC in 1997 (EC 1997). Pane casareccio di Genzano is made from wheat flour using the sourdough process. The bread is shaped into either round loaves (Figure 40.3b) or long broad baguettes. The production process fixes the raw material amounts (sourdough, water, and salt) in bakers % (flour = 100%). The traditional process includes three steps. The initial operation is the preparation of the sourdough. After the first fermentation of about 1 h, the bread is formed and then left to leaven on hempen cloth inside special wood cases for another 40 min. Baking is carried out in wood-fired ovens at 300–320 °C/572–608 °F for 35–80 min according the bread size (from 0.5 to 2.5 kg); in these conditions, the crust (about 3 mm thick) is formed and the crumb keeps moist. The crumb texture presents some large bubbles, typical of sourdough bread (see Table 40.2).

The origins of this product are related to the peasant culture of the production area: every household used to make its own bread (in fact *casareccio* means "made at home"). Pane casareccio di Genzano was already known and appreciated in the past century for its particular aroma and fragrance which last up to 7 or 8 days. Since the 1940s, the bread has become extremely popular in Rome were it is brought from Genzano at night and sold fresh the next day by local grocers and bakeries.

Pane di Matera

More recently, pane di Matera (Matera bread) has also been awarded the PGI designation (EC 2008). Visually, pane di Matera (see also www.panedimateraigp.it) is cone-shaped or "tall", each loaf weighing 1 or 2 kg, with a crust at least 3 mm thick and a pale yellow crumb with characteristic holes. Every stage in the production process, from preparation to packaging, takes place in the Province of Matera. As reported in the bread specification, in the production of pane di Matera the first step of the process is the preparation of the culture yeast (natural yeast) from durum wheat remilled semolina and fresh ripe fruit pulp that is kept in water, in a jute cloth until it doubles in volume over 10–12 h at 26–30 °C (79–86 °F). Flour is then added to the "mother dough" in the same quantity together with 40 % water. The addition of flour and water is repeated several times until a dough that rises in 3–4 h is

obtained. This culture yeast may be used up to three times to produce the final bread by adding 100 kg durum wheat remilled semolina to 20–30 kg culture yeast, 2.5–3 kg salt, and 75–85 L water. The ingredients are worked for 25–35 min and the dough is then left to rise for 25–35 min, covered with cotton or wool cloths to obtain an even leavening, avoiding the formation of a crust. The dough is then separated into 1.2 kg or 2.4 kg portions, roughly in the shape of the final product, to produce loaves weighing 1 and 2 kg, respectively. The loaves, which are shaped by hand, are then left covered with a cotton cloth on wooden boards for 25–35 min. After a final leavening period of 30 min, the loaves are baked in an oven fired with wood material (locally produced) or gas. In order to preserve its typical characteristics, pane di Matera can be packaged either in microperforated plastic, partly transparent to permit product visibility, or in windowed multi-layered paper, both of which display the bread and ensure a shelf-life of at least one week.

Pane Toscano

This is one of the most well-known breads outside its production area. Pane Toscano distinction consists in the lack of salt in the formulation, a tradition that dates back to the 12th century following the block of salt sale imposed by the Pisan authorities during the bitter battles between Pisa and Florence. The raw material is common wheat flour which is mixed with sourdough in a ratio of 70 : 30. After a long leavening time which gives an irregular cellular structure to the crumb, the dough is formed into a large baguette, or more commonly into a loaf, weighing between 0.5–1.5 kg ([Figure 40.3c](#)). The strong links that tie this bread to the region and its history justify the increasing interesting for obtaining the PDO mark from the European Union.

Coppia Ferrarese

Coppia ferrarese obtained the European PGI mark in 2001 (EC 2001). This bread has the particular shape shown in [Figure 40.3d](#): two ribbons of dough knotted together in the center with the ends twisted to form four spokes, called *crostini*. Each loaf weighs up to 200–300 g. The standard specifies the several steps of bread making. The raw material is wheat flour. The sponge and dough process requires a first leavening of 3 h. The final dough (which can contain olive oil) is divided into 20 cm strips which are folded into a spiral form by the skilful movement of the baker's fingers and palm. The bread is baked at 210–230 °C/410–446 °F for 20–25 min. The product is quite crispy and friable with little crumb and small bubbles in the four spokes and presents larger cells in the central part where the spokes join, as shown in the detail in [Figure 40.3d](#).

This folded bread is an integral part of the culture and history of Ferrara: as early as 1287, communal statutes compelled the city's bakers to produce bread in the shape of scrolls (*orletti*), which evolved into the modern shape. These rules stated that the weight of the loaf had to remain unchanged after baking, and penalties were set for bakers who did not respect these guidelines. There are several citations of earlier forms of coppia in the accounts of the rich Renaissance banquets at the court of Ferrara (not far from Bologna).

Michetta

This is the Milanese bread par excellence. It is obtained with wheat flour and using a sponge and dough process. The sponge is allowed to rest for 18–20 h. The dough is divided into

regular pieces by using a specific cutting machine that gives the rolls their typical shapes with a special mold. The finished product has a friable crust and a crumb with equal size alveoli, or a single large bubble in its interior *(Michetta soffiata)* if baked at high temperatures ([Figure 40.3e](#)).

Pane Carasau

Pane Carasau is also very well-known outside Sardinia and it is also known as "*carta da musica*" (music paper) due to the particular sound produced during chewing. Originally this bread was produced mainly in the internal areas of Sardinia. Today it is produced by bakeries all over the island (Dettori and others 2002).

It is a round-shaped bread about 40 mm in diameter and 1–2 mm thick, with no crumb ([Figure 40.6a](#)–[d](#)), made of "granulars", a blend of semolina and other coproducts obtained from durum wheat milling (Dettori and others 2002). Its long shelf-life is related to the double-baking process which dramatically reduces the final humidity of the product to about 6%. This characteristic has made Pane Carasau the most important food for the shepherds who lived away from their families for up to 5–6 months without being able to acquire fresh bread (Bordo and Surrasca 2002). It is traditionally obtained by a sourdough process, mixing 45 L water, 1 kg natural yeast (called *framentarzu*), and 2 kg salt per 100 kg granulars of durum wheat. The few existing studies on the properties of the semolina used for this process emphasize how important it is to use semolina with intermediate protein characteristics, especially for the elasticity indices expressed using the Gluten Index (Dettori and others 2002).

(a)

(b)

(c)

(d)

(e)
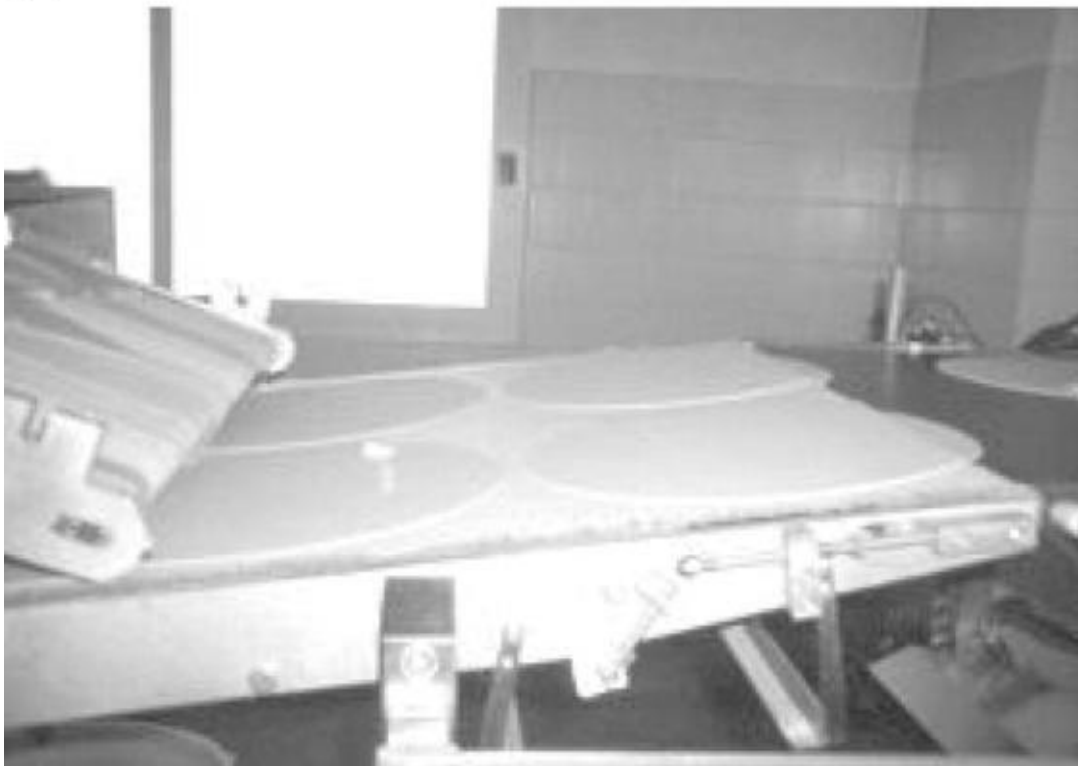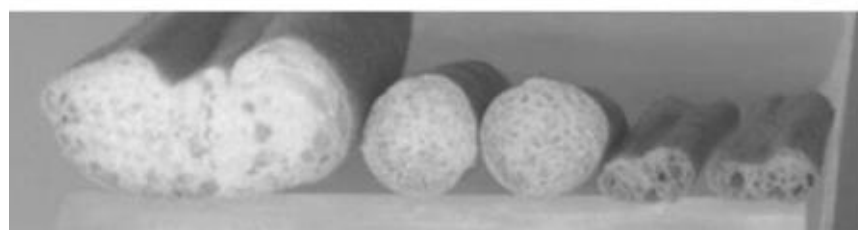
Artisanal *grissini*

Figure 40.6 Process flow chart and final characteristics for typical Italian crispbreads. Pane Carasau: production of sheeted disks (a), formation of a bubble during the first cooking step (b), cutting of the bubble in two disks (c), final product after the second cooking step (toasting) (d). Grissini: artisanal (e) and industrial (f), the whole products and their sections. Arrows indicate the stretch breadsticks.

The dough has an initial fermentation (at 28–32 °C/82–90 °F for 1 h) and then is sheeted to obtain disks (Figure 40.6a) which are put on cotton or flax cloths, piled up, covered and made to rest for about 2 h. They are then baked at very high temperature, 560–580 °C/1040–1076 °F for a few seconds. Due to the flash-evaporation of water, the round sheet swells immediately into a large bubble (Figure 40.6b). It is immediately taken out of the oven, cut along the edges, and the top divided from the bottom (Figure 40.6c) to obtain two symmetrical sheets. These disks are then baked and toasted for 15–20 s at 400 °C/752 °F (Figure 40.6d).

Grissini

Grissini or breadsticks (Figure 40.6e, f) firstly appeared in Turin (the Piedmont region). This particular bread probably dates back to the middle of 14th century and was certainly known by Napoleon. The origin of the word is Piedmontese and derives from *grissa*, a general term for the loaf. The transformation into its present form seems to be linked to the particular economic conditions existing in the region during the 14th century that required the sale of very light bread, a characteristic assured by the low humidity after baking at 250 °C/482 °F for 10–15 min. The so-called *grissino stirato* (stretch breadstick) is made with lard or olive oil. Baker's yeast is used for the leavening which requires 90–120 min. In the artisanal process, the dough is cut into strips, rolled between the fingers, pulled into shape and then baked in a preheated oven to obtain the final product.

Italian pizza and similar products

As is well-known, pizza is prepared from a dough made of wheat flour, water, and yeast worked to get a flat shape, which is variously topped and baked. Although it is now a common product all over the world, pizza is generally considered an original dish of Italy, and especially the Naples area.

Pizza has a long, complex, and uncertain history. The first written record in *Latin vulgaris* of the word pizza (*piza*) dates back to the year 997. Before the 17th century, pizzas were topped with lard, garlic, and coarse salt; afterwards, the lard was replaced by olive oil and the recipe enriched with fish. At that time, it was considered a food for the peasants and the poorer classes. In 1889, in honor of the Italian Queen Margherita of Savoy, the chef Don Raffaele Esposito created the pizza Margherita topped with tomatoes, mozzarella, and basil to represent the colors of the Italian flag. Until the beginning of the 20th century, the pizza and pizza stores were a purely Italian phenomenon, mainly Neapolitan, but gradually – in the wake of emigration – this product began to spread abroad to different countries. In the early 1900s, when Italian immigrants passed through Ellis Island, they brought their pizza recipes and skills with them. Only after World War II, adapting to the tastes of different countries, did pizza become a worldwide phenomenon.

Artisan products

The European Commission recently awarded the Traditional Specialty Guaranteed (TSG) label to pizza made with the traditional Neapolitan recipe (EC 2009b. *Pizzerie* (pizza shops) selling Neapolitan pizza (*pizza Napoletana*) in Europe that wish to use the TSG label must conform to a series of rules regarding not only pizza preparation and cooking, but also the use of ingredients from the Italian tradition.

According to the new ruling based on the traditional recipe, the pizza Napoletana must be round and have a diameter of < 35 cm, a raised golden-brown border, 1–2 cm wide (Figure 40.7). The consistency of pizza Napoletana must be tender, elastic, and easily foldable. The pizza must be covered with tomato (perfectly blended with extra virgin olive oil), *mozzarella di bufala Campana* PDO *(*PDO buffalo milk mozzarella from Campania or Mozzarella TSG) in close and evenly-spaced blobs, with oregano and fresh basil, that, combined with tomato, lend the pizza its delicate and characteristic fragrance. The dough rising is performed in two different steps: the first takes 2 h on dough taken from the mixer and covered with a damp cloth, the second lasts for 4–6 h, once the dough balls have been formed. After shaping, cooking must take place exclusively in a wood-fired oven with a baking temperature of about 485 °C/905 °F.
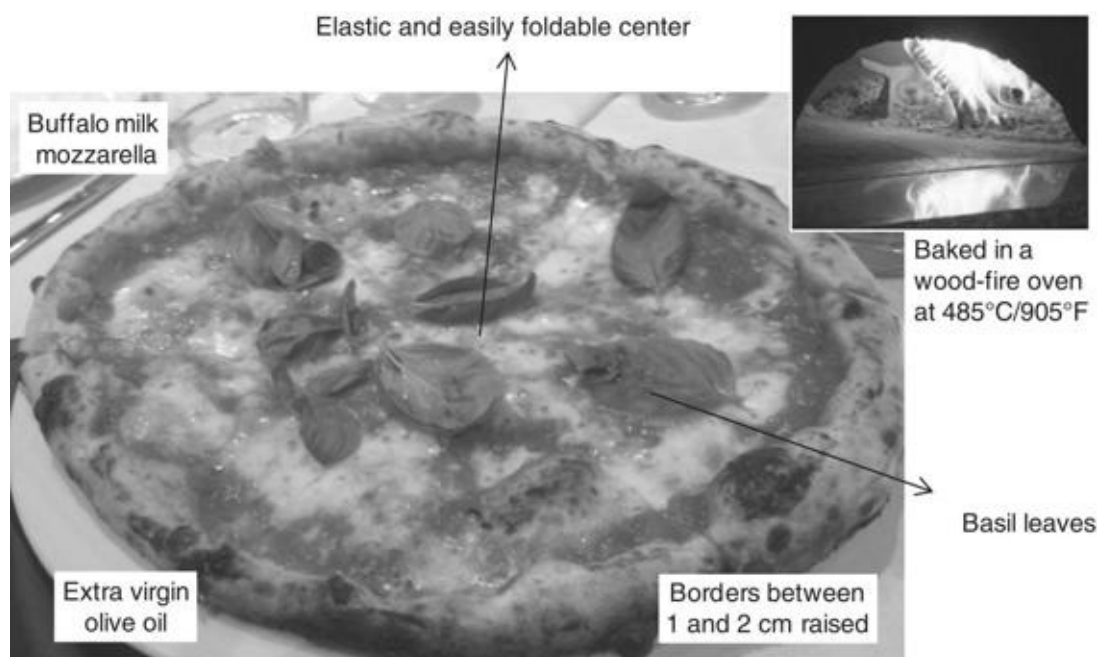
Figure 40.7 Shape and characteristics of Neapolitan pizza.

Besides Neapolitan pizza, there are numerous popular varieties of pizza made in Italy along the entire peninsula. Some of them belong to the tradition of different Italian regions and their origins date back to the 20th century. In the 1930s, 'metro pizza' (*pizza al metro*) was created near Sorrento. It has the same preparation of round pizza, but is obtained with a much larger amount of dough and is seasoned with different types of ingredients to have several toppings placed on the same pizza base. The 'metro pizza' is baked in very long wooden ovens given the length of this kind of pizza, which often exceeds 1 m.

Another traditional product – the *focaccia di Recco con il formaggio* (Recco focaccia with cheese) – has recently obtained the PGI designation (only for the Italian territory), pending registration from the European Commission (Italian Legislation 2012). It consists of a double layer of a paper-thin, almost transparent dough filled with a layer of a particular fresh cheese called *stracchino* or *crescenza*. After spreading the cheese, the border of the upper dough layer is pressed to seal the two layers together, some cuts are made on the surface of the focaccia, which is then brushed with plenty of extra virgin olive oil and sprinkled with salt before baking. Cooking takes place at about 250 °C/480 °F for 12–15 min. The focaccia must be eaten while it is still hot and the cheese is still creamy.

Industrial products

Nowadays, in addition to the huge number of pizzas made by artisans, there is a growing demand for industrial pizzas sold in the ready-to-eat market of frozen foods.

The characteristics of this type of pizza strongly depend on the raw materials used for both the base and the toppings and on the production process that, in the case of frozen pizza, also includes a freezing step, frequently performed with air-blast freezing equipment. The partially baked frozen pizza is definitely the ready-to-eat dish that is experiencing the greatest commercial success both in Europe and worldwide (Favalli 2008). Different formulations and technologies are used to prepare the bases for this pizza on an industrial scale.

Artisan style base (from laminated dough pieces). This is the best known and most widespread shaping process that creates a product quite similar to that produced in the pizza

shop. The appearance is a slightly irregular disc with a central thickness of 0.3–0.5 cm and a raised edge (1.0–1.4 cm). It is produced starting from a dough similar to the one used for bread production (2–4 parts of fat to 100 parts of flour) by adopting a straight dough or a sponge and dough process. The final dough is divided into a small ball weighing 180–230 g, depending on the desired base weight. There follows a leavening phase, generally performed at 35 °C and 65% RU for a period of 50–90 min, and then the dough sheeting operation through paired rolls, performed in two different directions to give roundness to the base. The most suitable flour to use for these products has a W value of about $300–320 \times 10^{-4}$ J (Favalli 2008).

Molded base (from laminated dough). This technology gives a base with a perfectly round edge due to the cutting procedure. It is generally prepared from a straight dough containing a higher amount of fat (about 5–8 parts to 100 parts of flour), which may include some leavened dough scraps. The dough is divided into large portions (25–30 kg), laminated by passing it through a series of rolling cylinders, left to rise for a short time (15–20 min at about 40 °C), and then cut through with particular punching blades into different required shapes and dimensions. Part of the laminated and fermented dough is then recovered and sent back to the kneading machine.

Thin and crispy base (from pressed dough) This kind of base is produced from a small dough portion produced with a rather weak flour ($W = 180 \times 10^{-4}$ J) to limit the elasticity of the dough and prevent its recovery after pressing. In fact, base shaping is not obtained through lamination but by means of a hot mold that presses the dough to 3–4 mm thick. With this technology, by using a mold with a diameter smaller than the finished pizza, it is also feasible to obtain a final product with higher edges than the central part, thus mimicking the artisan style pizza (European Patent 2006).

Once the pizza bases have been cut out, the topping is added. Tomato sauce, cheese, herbs and spices, and other toppings such as salami or ham are automatically spread over the pizza bases. Often garnishing, excluding tomato sauce and in some products cheese, is placed over the pizza bases after baking. Once the topping has been applied, the pizza is ready for further processing. Depending on how the pizza is to get to the end consumer, the steps following may differ. Whether deep-frozen, pre-baked and then deep-frozen, or fully baked and then cooled – each type of pizza has its own process.

As for many other types of baked products, pizza can be baked with different types of ovens, generally with horizontal tunnels, thus performing a continuous operation. Generally, pizza is baked an oven temperatures ranging from 250 to 350 °C/480 to 662 °F. The most common heating system and transfer equipment are indirect ovens (Cyclotherm ovens), in which the combustion fumes are forced inside tube exchangers placed below and above the conveying belt. In this type of oven, heat is transferred to the product mainly by irradiation, but convention and conduction also play a certain role. Baking time can be varied by changing the speed of the belt and modifying the temperature diagram of the oven. In other types of ovens (direct ovens), direct contact between the dough and the combustion gases is achieved. Heat exchange can be further improved by forcing the air to circulaten over the pizza bases. In the wood-fired tunnel oven made of firebrick material, pizzas are placed over a serpentine shutter conveyor belt to reproduce the characteristics of the traditional stone. Two combustion chambers, powered by wood and connected to the baking tunnels through slits, are located on both sides of the conveyor belt.

The final operation is often freezing, generally following a blast-chilling step aimed at reducing the product temperature to −12 to −14 °C. Self-stacking spiral freezers such as the Frigoscandia GYRoCOMPACT equipment, which can also be used to completely freeze the product, are commonly used for this operation. Before freezing, it is also common practice to spray some water over the toppings to prevent their detachment from the base. After packaging, the pizzas are then stored at temperatures lower than −18 °C to complete product freezing before shipping.

Sweet baked products

This category includes baked products that were originally associated with festive occasions because the formulation was enriched with prime quality ingredients, in particular sugar, butter, and eggs. These ingredients guarantee specific and much appreciated sensory properties (aroma, taste, and palatability) and at the same time provide new and specific rheological properties to the dough.

The Italian sweet baked products sector includes many artisan bakeries and pastry stores and some industrial companies. The division by product type highlights the particular situation of the soft products sector. This includes the industrial production of *Panettone, Pandoro*, and *Colomba*, the traditional "festivity cakes" mainly consumed at Christmas or Easter, and obtained by the sourdough leavening process similar to that used by the artisans, and the so-called "serving-size products" (monodose or merendine in Italian). The formulation of the latter products can differ widely but all are characterized by the size, usually 35–50 g, ideal for a snack between meals or for breakfast. This market category represents approximately 20–25% of the total production of this sector. Sweet bakery products companies originally introduced serving-sized products to rationalize their production over the year. The category is now also of interest outside Italy.

Classification of Italian sweet baked products

Diversification in the sweet baked products sector is still much greater than in the bread sector due to the significant variation of the ingredients other than flour and water that can be used. Each region has its own characteristic sweet products with formulations that include ingredients typical to that agronomic area (Bordo and Surrasca 2003). Sardinian products provide an interesting example. Because it is more readily available than common wheat flour, remilled semolina from durum wheat is still used, together with honey and concentrated grape-must (called *sapa*) as alternatives to sugar. This basic recipe can be flavored with grated lemon and orange rind and spices and formed as a small pocket for *pistiddu*; it can be enriched with almonds, obtaining the so-called *papassino*, or candied fruits (mainly orange) and nuts, obtaining *pani 'saba*. Grape-must is also frequently used in central-southern Italy where vine cultivation is widespread.

Other very similar recipes can be found in different areas of the country. For example, *amaretti* (see the process card) have an almond base and are traditional products of many regions of northern, central, and southern Italy (Bordo and Surrasca 2003).

A universal classification criterion used for sweet products is based on the richness of the sugar and fat formulation, measured according to their quantity to 100 parts of flour. The distribution of various Italian traditional products according to this approach (Figure 40.8) highlights the overlaps that can unexpectedly occur, such as between the Panettone or Colomba and Pandoro (famous soft cakes – see the process cards) and a number of high friability products, such as cookies and cakes obtained by short dough.
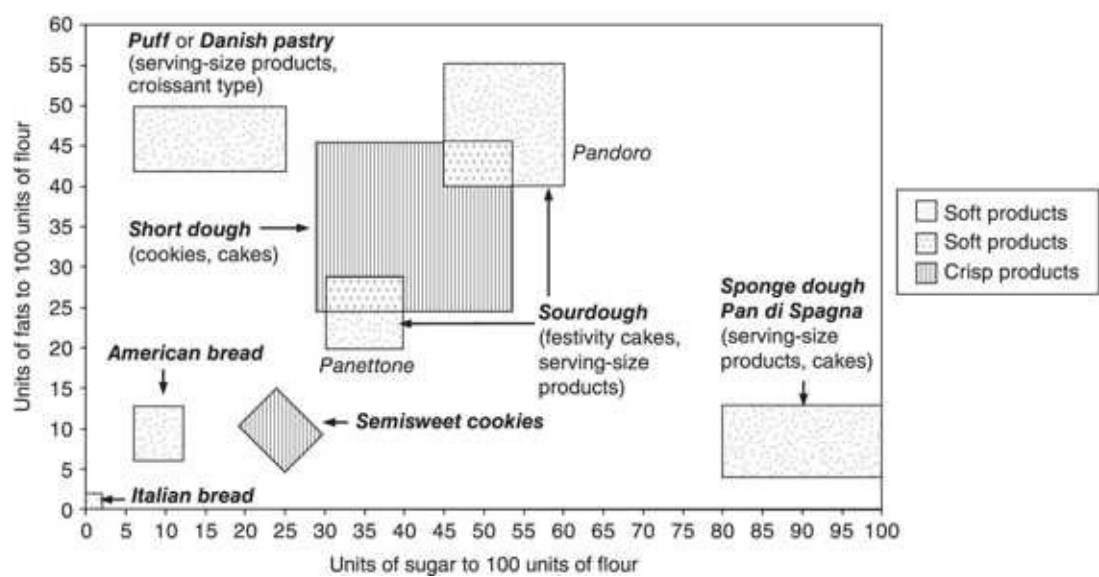
Figure 40.8 Baked products mapping on the basis of sugar and fat content of the formulation.

Although the formulation of baked products is important for ensuring palatability and other important sensory properties, it represents just one of the variables that can influence the texture of these foods. To perfect the classification of sweet baked products, we must consider the conditions used during each phase of the technological cycle and their influence on the formation of the bubble structure. With sweet baked products, as opposed to bread, it is also possible to use non-biological methods for leavening (see Figure 40.1).

Water content plays a key role in obtaining the peculiar structural properties of the dough. To obtain a final soft texture, the water content of the dough needs to be 25–35%, an amount which is contributed to by liquid ingredients such as eggs, as shown in Table 40.4. These conditions provide a homogenous hydration of all the hydrophilic components during mixing together with the gelatinization of the starch during baking, a phenomenon that plays a significant role in the final texture (Godon 1994). According to the leavening method used to obtain a porous structure, the dough has such diverse properties that it assumes a specific name as a function of the technological process used. In soft, tender sweet products obtained by biological leavening, the accumulation of CO_2 produced by the yeasts occurs gradually over a long period of time (several hours). A regular, homogenous gluten network must be developed, preferably using the sourdough process previously described for bread. The critical ingredient in these processes is the type of flour used, which must be selected according to its rheological characteristics. Strong flours are especially suitable (Calvel 2001, Pagani and others 2013) because they contain proteins able to withstand the physical stress of the process such as repeated mixing and kneading (which must be performed in mild conditions) and the pressure created by the leavening CO_2. The long biological fermentation times lead to substantial porosity and frequently to the formation of many alveoli of different sizes, formed when the smaller bubbles coalesce, a phenomenon already described for sourdough bread (van Vliet 1999).

Table 40.4 Classification of Italian sweet-baked products on the basis of formulation and process

		Soft products with high porosity		Crisp products with high friability	Other products	
		Dough	Batter	Short dough	Mixture	
Main ingredients (%)	Flour	100	100	100	High variability of components and generally without wheat flour	
	Sugar	30–50	80–100	30–60		
	Fat	20–50	0–10	20–60		
	Egg	20–50	40–100	0–5		
	Other	0–25	0–25	0–30		
Dough humidity (%)		25–35	30–35	10–15	High variability	Low moisture <5
Gluten development		Complete	Partial	Partial	No development	
Leavening		Biological (sourdough)	Chemical and/or physical	Chemical	None	If present, physical

Final product: *humidity (%) water activity* (a_w)	18–24	18–20	2–15	High variability	<10
	0.75–0.83	0.75–0.81	0.70–0.78	High variability	0.20–0.55
Specialties	**Festivity cakes** Panettone, Pandoro, Colomba, Pandolce, Bisciola Serving-size products	*Pan di spagna* (*sponge cake*) Serving-size products	**Typical cookies** Krumiri, offelle, baci di dama Serving-size products *and* cakes Sbrisolona Short pastry of Pastiera, Cannoli, Pardulas	*Panforte* (H_2O = 12–14%) (a_w = 0.65) *Castagnaccio* (*chestnut cake*) (H_2O = 52–54%) (a_w = 0.95)	*Amaretti (physical leavening due to whisked egg whites)* **Pasta di mandorle** and **Marzapane** (no leavening)

A soft texture with a fine grain can be obtained by inserting a high quantity of air in the mass during mixing using high-speed mixers (physical leavening), which raise the specific volume of the mass to values similar to those obtained with biological fermentation. The creation of a light texture is completed during the baking step by the development of CO_2 derived from the reactions between the salts of the baking powder (chemical leavening agents). Thus, the rising capacity of the batter (a specific term for dough with a very low consistency) derives from the emulsifying substances that stabilize the numerous air bubbles incorporated during the high-speed mixing phase and provide a fine cellular structure (Pyler 1988). In these products (known as *Pan di spagna* – sponge cake), the structural component is not gluten (in fact "weak" flours are particularly favorable) but egg proteins. This type of texture quickly breaks down without resistance when chewed. Depending on the Italian geographic region, the basic recipe (sugar, eggs, flour) can also include raw materials such as cocoa, almonds or ground hazelnuts, maize flour or other gluten-free cereals, and even grated apple or carrots. The recipe can also be made richer with the addition of coatings, icing and/or fillings, as reported in the latest publication by Bordo and Surrasca (2003). Some formulations have been applied on the industrial scale to obtain serving-size products which are briefly described in this chapter.

To obtain friable products (both cakes and cookies) typical of Italian tradition, it is important to form a short dough (Table 40.4), creaming the sugar and fats together and adding a small quantity of water (Figure 40.9). The specific rheological properties of these short doughs require a limited alveolar development obtained by the fast action of the chemical leavening agents during baking. Three types of cookies (*Krumiri, Ofelle* and *Canestrelli*) that are famous in north Italy are shown in Figure 40.9. This type of dough is also typical of the southern regions of Italy and is used as a "container" for products with delicious rich fillings based on fruit, jam, or dairy (*ricotta* cheese) (Bordo and Surrasca 2003). The most widely

known examples are the Sicilian *Cannoli* (the filling is composed of ricotta cheese and candied fruit) and *Cassatelle* (with a filling of ricotta cheese, sugar eggs, and cinnamon), the Sardinian *Pardulas* (with a filling of ricotta cheese, sugar eggs, semolina, orange rind, and saffron), and the Neapolitan *Pastiera*. The pastiera filling is composed of wheat kernels that, after a long soaking for 2–3 days and cooking in water, are added to milk, sugar, egg yolks, ricotta cheese, candied fruit, lemon rind, and cinnamon.
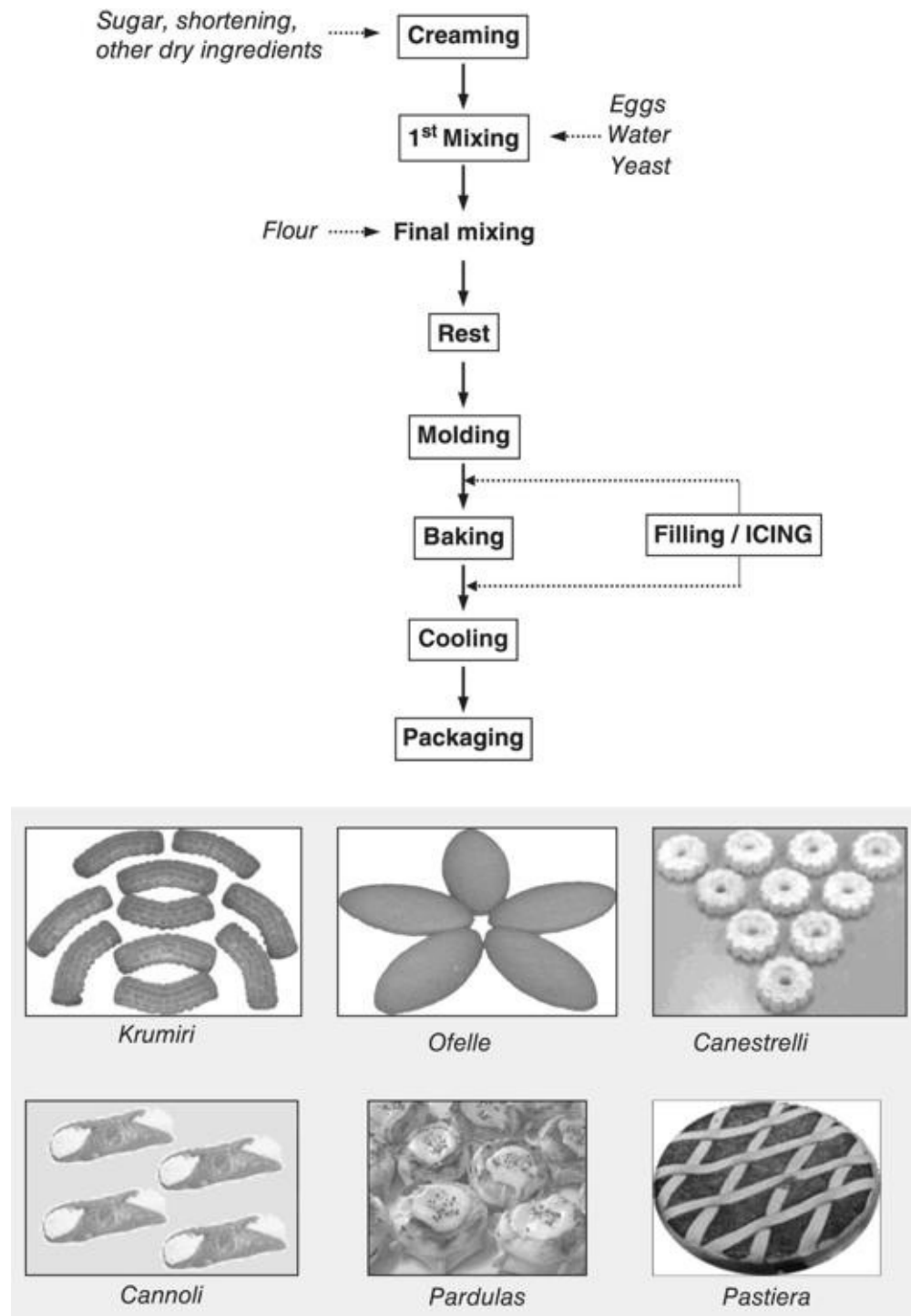
Figure 40.9 Process flow chart for the production of short dough cookies and filled pastry.

Finally, typical Italian sweet baked products can also fall into another category (Table 40.4), difficult to classify on the basis of the criteria in Figure 40.1, which lists products of ancient origins developed in some regions according to the availability of specific raw materials (some date back to the Middle Ages and the Renaissance). Although extremely diverse in consistency, most of these sweet products have a lack of wheat flour in common. For some of

these specialties (for example castagnaccio, see the process card), their tender texture is not due to the cellular texture but largely to the high water content (> 50%). Water is held by the constituents, particularly the gelatinized starch and other polysaccharides, that combine into a gel. The gel contains so-called "inert" substances, large ingredients (such as candied fruit, pine kernels, raisins) that cannot interact in a homogenous mass. Similarly, cohesion of the mixture in other products (amaretti, see the process card) of this category is not due to the presence of wheat flour protein but of thermocoagulable proteins such as egg proteins. Some of the most widely known Italian products listed in Table 40.5 are described here.

Table 40.5 Physical characteristics of typical Italian sweet-baked products[a]

Sweet-baked products	Leavening process	Moisture (%)	a_w	Weight (%)	Specific volume (mL/g)	Porosity[b] (%)	Large cells area[c] (%)
Soft							
Festivity cakes							
Pandoro	M	20–25	0.78–0.80	1000	4.5–5.0	30–35	1–3
Panettone	M	22–24	0.80–0.82	1000	4.0–4.5	35–40	25–30
Colomba	M	24–26	0.80–0.85	1000	3.5–3.8	32–34	30–40
Serving-size products							
Sourdough (**A**)[d]	M	15–18	0.78–0.80	40–45	4.5–5.0	28–32	10–20
Puff pastry (**B**)[d]	M/P	13–18	0.76–0.78	40–45	3.4–3.6	24–28	0
Sponge cake (**C₁**)[d]	C	18–23	0.78–0.80	38–42	1.5–2.0	28–31	8–12
Sponge cake (**C₂**)[d]	C	17–20	0.79–0.81	30–35	2.0–2.2	22–24	28–30
Sponge cake (**E**)[d]	C/P	21–23	0.78–0.80	30–35	3.8–4.2	26–30	absent
Not leavened cakes							
Castagnaccio	absent	52–55	0.94–0.96	1000	0.9–1.1	none	absent
FRIABLE							
Cookies							
Ofelle	C	2–3	<0.1	11–12	1.3–1.5	lower than 15%	absent
Krumiri	C	1–2	0.26–	10–11	1.2–1.5		

			0.28				
Canestrelli	C	3–4	0.21–0.23	8–9	1.3–1.5		
Amaretti secchi	C	2–4	0.18–0.20	3–4	3.2–3.4		
Amaretti morbidi	C	9–11	0.52–0.56	18–20	1.5–1.7		
Serving- size product							
Pie crust (**D**)[d]	C	5–7	0.62–0.66	46–48	1.2–1.5	<15	absent
Not leavened cakes							
Panforte	absent	12–14	0.62–0.64	400–500	0.9–1.0	none	absent

[a]Unpublished data.

[b]Cell area/total area.

[c]Cell with area higher than 25 mm^2/total area.

[d]The capital identifies the product shown in Figure 40.12.

M, Mother (sourdough); C, chemical leavening; P, physical leavening.

Festivity cakes

The most well-known Italian festivity cakes are Panettone, Colomba and Pandoro (see the process cards) together with other similar regional cakes such as *Pandolce* from Liguria, *Bisciola* from Valtellina (Lombardia) and *Pani'e saba* from Sardinia (Bordo and Surrasca 2003). These cakes all belong to the same commodities sector from the point of view of sales and similar purchasing motives, and from the technological point of view, due to the great similarity of their production cycles, which require the use of natural sourdough. They can be defined as leavened enriched breads since they undergo a biological leavening which is usually performed by particular *Saccharomyces* species present in the sourdough in symbiosis with lactic acid microflora (Galli and Ottogalli 1973; Galli and others 1988), giving light products characterized by a high specific volume, as for bread (Table 40.5).

As already stated, for the types of breads obtained using sourdough, the natural microbial inoculum is perpetuated through a cycle, which, according to the conditions of the process used, requires from 20 to 36 h of preparation, mainly to obtain the full sourdough (Figure 40.10). The seed sour (from a previous dough) is left to ferment under controlled conditions, often tightly wrapped in a cloth. This method maintains high CO_2 content in the mass, thus lowering the redox potential and enabling heterolactic fermentation to take place (Foschino and Galli 1997).
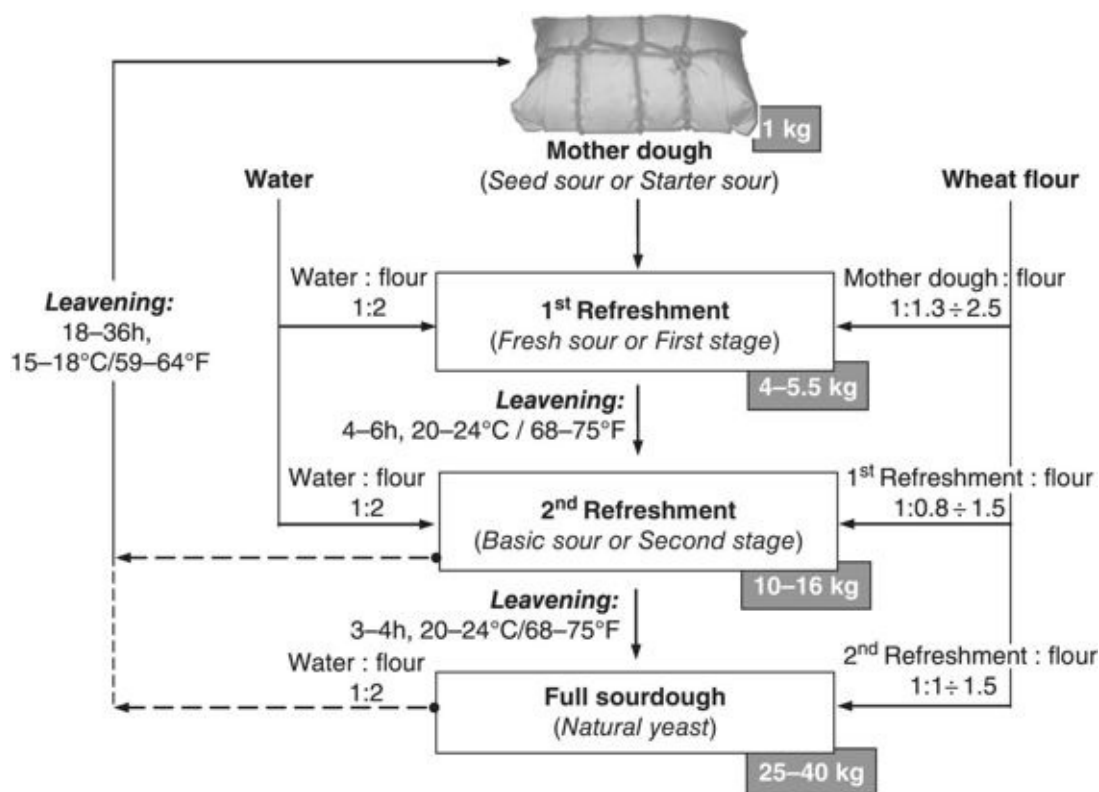
Figure 40.10 Multistage process for sourdough production for Italian sweet baked products (as Pandoro, Panettone and Colomba). In each step, the more frequent ratios of the ingredients (flour, water) are indicated; the conditions of fermentation are also reported. The "mother dough" or "seed sour" can be taken either from the "2nd refreshment" or from the "full sourdough" steps.

The lactic flora of the mother dough contains the same species found in seed sour used in bread making (Galli and Ottogalli 1973; Galli and others 1988; Ottogalli and others 1996), where *Lb. sanfranciscensis* or *Lb. brevis* var. *lindneri* are usually present in a strict association with *S. exiguus* or *Candida holmii* (Foschino and others 1995). As previously discussed for the sourdough bread, the microbial metabolic activity causes a sharp decrease of the pH (that can reach values lower than 4), and a significant increase in acidity, creating a selective environment from the microbial point of view that is rich in those metabolites responsible for the peculiar sensorial properties of the finished product (Ottogalli and others 1996).

In general, there are three refreshment phases of the sourdough using the addition of water and flour, which gradually increases the leavening mass to obtain the full sour and to maintain the quality-quantity ratio of the microorganisms unaltered (Vogel and others 1996). The seed sour usually represents 5–15% of the ingredients that make up the full sourdough, less than in bread sourdough. Although there are no detailed studies on the subject, the ratios of ingredients (flour, water, mother dough) given in Figure 40.11 are those most frequently used in industrial processes since they maintain a correct ratio between the lactic and acetic acid concentration and between the LAB and the yeasts. The microbial starters, frequently used for the production of wheat or rye bread (Stolz and Böcker 1996; Kulp 2003), are not used either at the industrial level or by artisan bakeries for making leavened enriched breads because this method does not guarantee satisfactory sensorial characteristics in the finished product (Lucisano and others 2003).
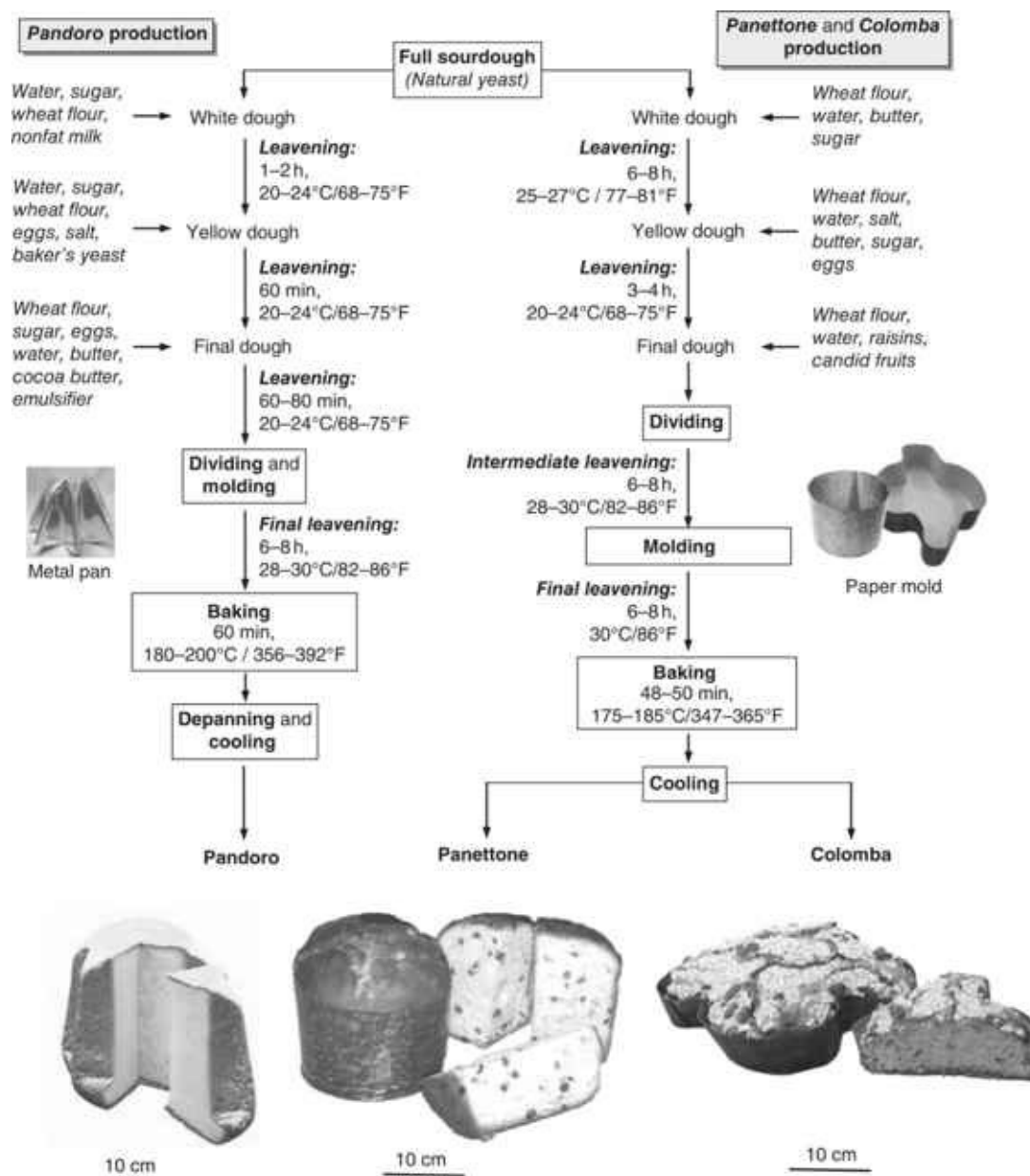
Figure 40.11 Process flow chart for the production of Pandoro, Panettone, and Colomba (from full sourdough to final product). The weight of the baked products is about 1000 g.

The refreshment phases, exclusively of flour and water, provide a dough with a well-developed, homogenous, viscoelastic gluten network that effectively contains the CO_2 produced during the final leavening phase when the final dough is placed in the mold (Figure 40.11). The sugar and fats of the recipe, which give rise to a shortening effect when present in high percentage (Calvel 2001), are gradually added after a continuous gluten network has been formed. At least three dough steps are required, with a rest between each for the leavening phase. The dough names reflect the ingredients added: the "white dough" contains sugar and fats while the "yellow dough" also contains eggs. Candied fruit and raisins, which significantly interfere with the viscoelastic properties of the mass, are not added until the last dough step, just before the dividing step.

Although the production cycles of Pandoro, Panettone and Colomba can be considered quite similar, important differences in their formulation are highlighted in Figure 40.11. Because of the high quantity of fat in Pandoro (about 22–27% of the final dough composition), baker's yeast is often added to the yellow dough to facilitate rising during the final long leavening period in the pan. Baker's yeast is not added to Panettone and Colomba (about 10–15% fat in

the final dough), where the only leavening agents are the yeasts from the seed sour, which multiplies during the refreshment phases. One of the most delicate phases for all products is the final dough step when the dough is divided, shaped, and molded. This process must be made with stress-free machines to prevent excessive stretching and compression. Thanks to the rich formulation of sugars and fats and the packaging methods used (polypropylene bag and cardboard box), the shelf-life of these products is approximately 6 months.

The Italian association AIDEPI (www.aidepi.it), that represents the most important companies of sweet baked products, has issued detailed processing standards for Panettone, Pandoro, and Colomba, the most important enriched leavened breads from an economic point of view. These standards (Italian Legislation 2005) not only describe the compulsory ingredients of the recipe but also each process phase.

Serving-size products – "merendine"

Of the most consumed baked products in Italy, the so-called "merendine" deserve special attention (Figure 40.12). These may be considered an interesting and recent industrial transformation of a number of traditional baked products produced at the artisan or domestic level. These foods, with the exception of the *croissant* and *brioche* in France, are common only in Italy, and date back to the 1950s, when one of the most famous festivity cakes companies introduced a "miniature" version of the Panettone on the market.
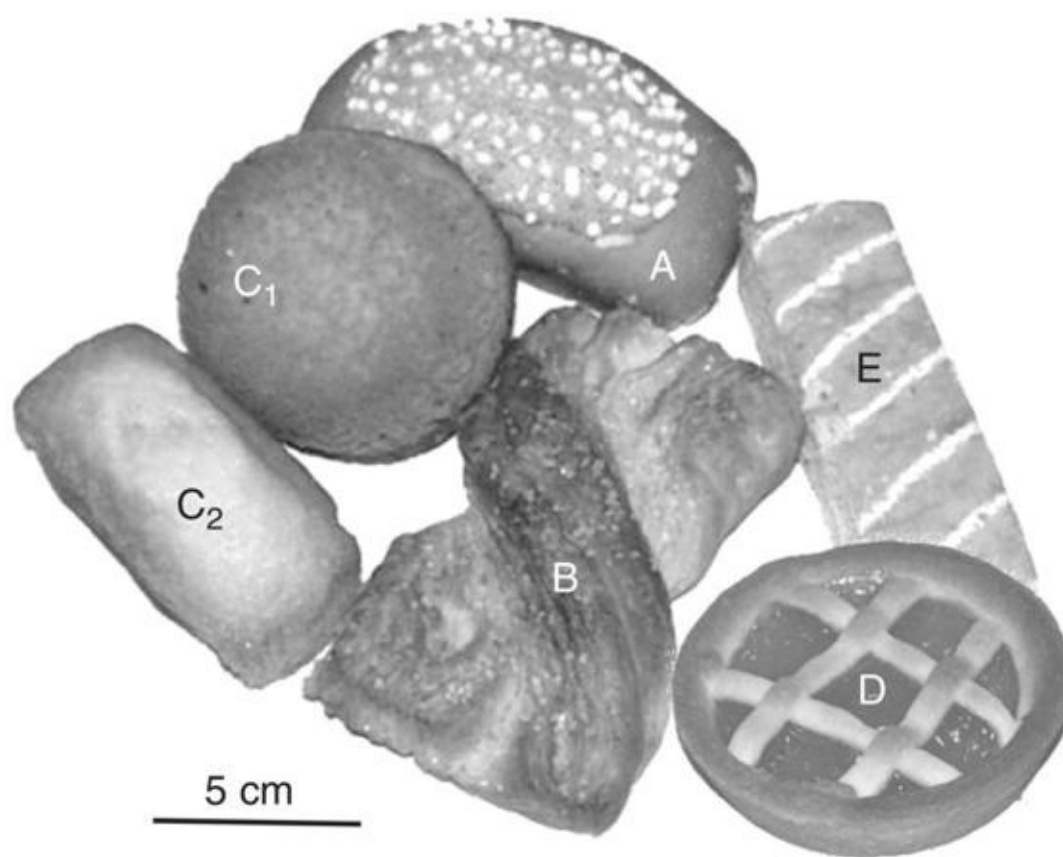
Figure 40.12 Typical Italian serving-size products (merendine): sourdough fermentation (A); puff pastry or Danish pastry (that is, sourdough fermentation plus physical leavening) (B); short pastry with chemical leavening (C_1 and C_2); pie crust (D); sponge dough (physical and chemical leavening) (E).

The common characteristic of these cakes is their weight, which does not normally exceed 50

g. They are packed in single portions, which helps maintain their sensorial characteristics for several months. These products are therefore an alternative to cookies and cakes, both for breakfast and as a snack, which in Italy and other Mediterranean countries is considered a meal, albeit a light one (FOSAN 2003). These Italian bakery products have little in common with the so-called sweet and savory snacks consumed in Anglo-Saxon and north European countries where, due to different eating habits, there has been a "destructurizing" of meals which has led to frequent eating outside the home. The consumer target is mainly represented by young people between the ages of 5 and 14 years, but these products are also appreciated by adolescents and adults.

The range of merendine on offer includes products obtained using a biological leavening process, almost always sourdough or puff pastry (physical leavening of a laminated sourdough), and a chemical or physical/chemical leavening process. The different methods of creation of the porous texture justify the diversity of the physical properties of these cakes (summarized in Table 40.5) and the fact that they can be classified both as soft products and as crisp, friable products (see Figure 43.1 and Table 40.4). Another significant aspect is the simplicity of the recipe, generally without the creams or fillings, high percentages of which can be found in snacks consumed in Anglo-Saxon countries (FOSAN 2003).

Process cards of typical Italian sweet baked products

Panettone

The Panettone, the traditional soft texture Christmas cake of Milan has its origins in the past. It is said that it was first presented in Renaissance times at a court banquet given by Federico il Moro.

Without doubt it is the most widely-known Italian baked product abroad. The Panettone has a cylindrical form (Figure 40.11) with a cracked upper crust cut in the characteristic shape of a cross (called *scarpatura)*, a very light internal texture with an elongated cellular structure, and a typical sourdough aroma. As opposed to the various products of the Verona school (Pandoro), the Panettone sourdough normally has a lower fermentation quotient (molar ratio between the lactic acid and the acetic acid). The fermented bulk dough is divided into individual pieces of predetermined weight and placed in a *pirottino* (the baking pan made of a special type of paper) for the final leavening (6–8 h) (see Figure 40.11).

The production standards issued by the Ministry of Productive Activities (Italian Legislation 2005) specify the compulsory and optional ingredients. The compulsory ingredients in the Panettone dough include eggs (either whole or yolks) – a minimum quantity of 4% yolks to the total mixture – and butter, which must total at least 16% (minimum percentages of the dry ingredients refer to the dough ready to be divided and net of raisins and candied fruit). Characteristic of this cake are the so-called "inert" ingredients, raisins and candied fruit, which make up at least 20% of the dry ingredients in the dough ready to be divided. Following the changes of consumer eating habits, especially those of children, recent formulations have been developed that do not contain inert substances.

Colomba

The Colomba (dove) is the typical leavened baked product produced at Easter throughout Italy, both at the industrial and artisan level. It dates back to 500–600 AD in Lombardy, with

its origins in both history and legend. It is said that it was created as a sign of peace to the barbarian invaders of the city of Pavia. On a par with the better known Panettone and Pandoro, this cake is made using sourdough. The technological steps for obtaining the final product (some of which are illustrated in Figure 40.13) are the same as for the production of Panettone except the final make-up (see Figure 40.11 and Figure 40.13).

(a)
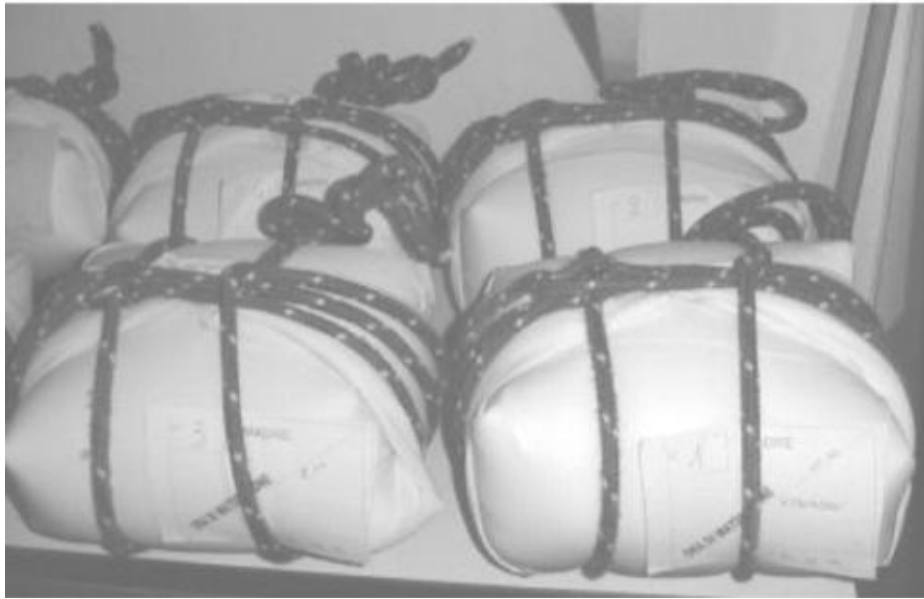
(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)

(j)

(k)

(l)

Figure 40.13 Main steps of Colomba production. Seed sour wrapped in a cloth during fermentation (a); full sourdough (b); "white-dough" formation using a spiral mixer (c); "white-dough" fermentation (d); ingredients of "yellow-dough" before mixing (e); final dough with candied fruit or raisins before dividing (f); dough pieces on curling belt (g); intermediate leavening of dough pieces on canvas pockets (h); dough in the paper mold – max dough height about 3 cm (i); dough after final leavening – max dough height about 5–6 cm (j); icing and decoration with sugar and almonds (k); final product after baking – max product height about 12–13 cm (l). The processing conditions of each step are reported in Figures 40.10 and 40.11 (Courtesy of Tre Marie, Milano).

It has an irregular shape like a dove, with a light texture and elongated porous structure with an icing of egg white, sugar, and hazelnuts and a decoration of sugar and almonds. According to the production standards issued by the AIDIPI industrial producers, the latter ingredient must represent at least 2% of the finished product. The minimum quantity of the other compulsory ingredients is the same as for the Panettone, with the exception of the candied

fruit – no less than 15% – made up exclusively of citrus fruit.

Pandoro

The Pandoro, the traditional Christmas cake of Verona (a town not far from Venice), probably got its name from its golden color, which is due to the high percentage of eggs and fat in its recipe. The first traces of its production date back to 1800. The Pandoro evolved from the Venetian antique Renaissance cake (*pan de oro*, golden cake*),* so-called because it was served in the houses of the nobility covered with fine gold leaf. There are also tales of a more humble origin. The ancestor of the Pandoro would seem to be a cake in the form of a star but with a more compact consistency, still popular and widespread (the *nadalìn*).

The Pandoro has a very soft dough which is obtained by natural fermentation. It has conical trunk form shaped into an octagonal star (see Figure 40.11). There is no external crust and it is usually covered with vanilla flavored icing sugar. The inside is silky with a fine, uniform grain texture, a characteristic obtained by the addition of baker's yeast (up to 1%) during the final kneading phases. The flour is added in increasing percentages during the different dough steps, as opposed to the Panettone where the amount of flour added decreases during each leavening phase. Finally the preservation conditions of the mother dough and the microbial species produce a minor accumulation of acetic acid in the dough. The production standard (Italian Legislation 2005) states that the eggs added to the dough (in the form of pasteurized whole eggs or egg yolks) must total not less than 4% of yolk of the total mixture, while the amount of butter must total at least 20% (of the dry ingredients in the dough ready to be divided). Vanillin is one of the compulsory ingredients of this cake. Fillings, toppings, frostings or other decorations can be added, provided that the finished product contains at least 50% of the basic dough calculated on the weight of the finished product.

Panforte

The Panforte is a specialty of Siena (central Italy) made with candied fruit (mainly candied citron and orange peel), toasted almonds or hazelnuts, sugar, honey, glucose syrup, and spices. It is traditionally a cake for Christmas, although in Tuscany it can be bought throughout the year.

It is a flat, dense, round cake on a starch wafer base, wrapped in a paper band and covered with a fine layer of icing sugar (Figure 40.14a). The name Panforte, "strong bread", is due to the strong, spicy flavor of the original recipe that dates back to 13th century. Spices were added to the original recipe of "pan melato" (honey bread) to increase the shelf-life of the cake. The most widely sold panforte today is *Panforte Margherita*, named in 1879 in honor of Queen Margherita, wife of the Italian king Umberto I, and based on a recipe which gave the cake a more delicate taste and a softer texture.

(a)

5 cm

(b)

6 cm

(c)
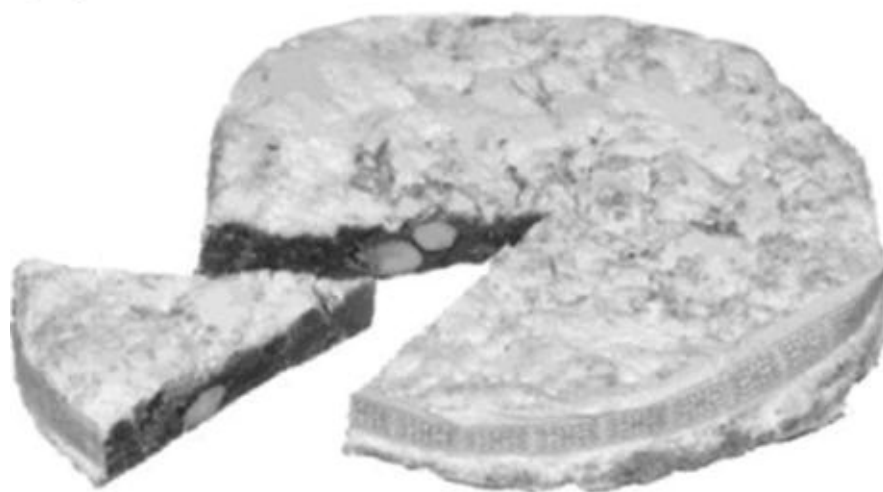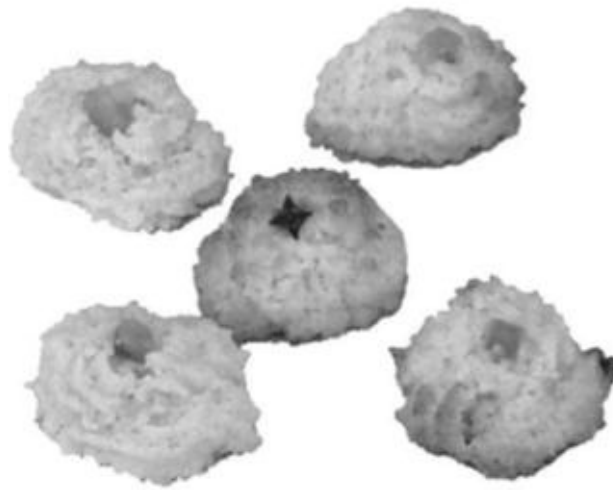
3 cm

Figure 40.14 Typical Italian cakes and cookies of the category "Other products" in Table 40.5: Panforte (a), Castagnaccio (b), Amaretti (c), Pasta di mandorle – artisan product (d); Pasta di mandorle (Ricciarelli) – industrial product (e).

The process comprises an initial phase of cooking the sugars, to which is added candied fruits which are cooked in the syrup. Whole almonds, flour, and spices are then added to the syrupy mass. The mixture is formed manually on a sheet of starch wafer and surrounded by a paper band. The cake is then baked in the oven at 210–220 °C/410–430 °F for about 15 min, and it takes on its characteristic consistency when it cools.

Castagnaccio

Castagnaccio (chestnut cake) is a humble dish that originates from traditional peasant cooking. It is made in Tuscany, especially in the autumn when chestnut flour is produced. The basic Castagnaccio batter is made of chestnut flour, water, olive oil, and salt, to which

other ingredients may be added according to where it is made, such as pine kernels, raisins, chopped nuts, candied orange, and rosemary. A liquid batter is prepared (water content higher than 53–55%), poured into low, wide pans and baked in the oven at 200–220 °C/392–430 °F for 40–60 min.

The Castagnaccio is ready when the surface is cracked and has an intense brown color. The finished product does not have a cellular structure and has a soft, compact texture ([Figure 40.14b](#)). It has a very brief shelf-life due to the high water content (higher than 45%) and a_w values higher than 0.9.

Amaretti and pasta di mandorle

Amaretti are dry pastry biscuits (less than 3% water content) that date back to 1400–1500, with a characteristic round shape, a cracked surface and a bitter almond taste ([Figure 40.14c](#)). According to the process standards of the AIDIPI companies, the basic, compulsory ingredients in the recipe for amaretti are sugar, a minimum quantity of almonds and/or apricot kernels (based on the dry substance of the final dough), and egg whites. The addition of flour (wheat and/or rice and/or maize) is optional. When present, this raw material must not exceed 12%. The presence of leavening agents is not compulsory since the porous structure is obtained from the air in the whisked egg whites. After mixing the ingredients, the batter is poured into mold bands.

Amaretti morbidi (soft amaretti) are also popular (also known as *Pasta di mandorle* – almond paste) ([Figure 40.14d](#)). The amaretti morbidi get their typical texture from their higher water content (8%) and from the higher quantity of almonds (at least 35%) set by the AIDIPI standard (referred to the dry substance in the final batter). Flour cannot be used, but honey and glucose syrups can be added.

From these basic recipes, amaretti and pasta di mandorle can be enriched with coverings and fillings as well as made into different shapes. In the dry product category, the so-called *Brutti e buoni* (ugly and good) are especially popular. They have an irregular shape and contain chopped hazelnuts, while the soft product version is called *Ricciarelli* (Bordo and Surrasca 2003).

Acknowledgments

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Mexican Bakery Products

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A brief history

Mexican bread is a fusion of different cultures due to the intervention of countries from Europe such as Spain and France. Bread arrived in Mexico from Spain in the 15th century with Hernán Cortés, his army, and his entourage. The local people (Indigenas) accepted this product, even though the corn tortilla was the traditional bread in Mexico at that time and continues to be so. The formulations used to manufacture bread in the New Spain (now Mexico) remain unchanged from that time, as do some names for Mexican breads despite the evolution of the Spanish language. The cultural shock was difficult because the taste, texture, and shape of maize tortillas were completely different to that of bread made with wheat.

There are some stories about the Mexican bread in the conquest time. One person named Juan Garrido (born in Portugal) participated in the conquest of Mexico with Hernán Cortés, and due to this he was given a plot of land close to Mexico City. Juan Garrido prepared food preparation for the Spanish army; one day while cleaning the rice seeds to eliminate stones and garbage, he found three wheat seeds. Juan missed the taste of bread and decided to plant the wheat seeds in a specific place on his plot; however, he thought that the wheat seed would not germinate, but after a few days he saw that a green shoot had emerged from the ground. The other two wheat seeds did not germinate. When the wheat plant was harvested, it produced 180 seeds, not enough to produce flour or make bread. Juan was patient and decided to plant more wheat seeds again. From the next harvest he obtained enough wheat seeds to continue the plantation and to prepare wheat flour and make bread. Wheat plantations were extended to other regions of the country and consequently bread was made elsewhere. The Mexican people started to eat wheat bread, but also learned to make it. To start bread manufacture, they built brick and clay ovens to conserve the heat produced from burning wood and coal. Additionally, the Mexican people invented diverse shapes, sizes, and formulations of bread and the types of bread grew.

The story of Mexican bread continued with the diversification of bread types. For example, due to the foreign invasions in the 19th century, as part of the last Europe colonialism, the Spanish invasion in 1829, and the French invasion in 1838 named "war cakes", other breads were adopted from those countries and modified with a Mexican feel. Political affairs such as the American invasion (1848–1849) introduced other bread types through the San Patrick's battalion formed by the Irish, and the French invasion (1862–1867) with the emperor Maximiliano, where a mixture of gastronomic styles (Austria, Italian, and French) were introduced and with this other bread types.

Mexican bakery industry

The bakery industry in Mexico is an important part of the culture and traditions, and Mexico is probably the country with the highest number of bread types worldwide. In accordance with international economic classification systems, the Mexican wheat industry is considered as a Manufacturing Activity, and a member of Division l: Food products, beverages, and tobacco. Furthermore, the wheat industry is composed of three subgroups: wheat flour, bread and cakes, as well as biscuits and pasta.

Currently in Mexico, there are more than 30 000 units of production at the national level, 92.1% operating in the preparation of bread and cakes, 7.4% biscuits and pasta, and 0.5% milling wheat. The size of the economic units is classified into: micro companies or family businesses that employ 1–17 people, representing 51.51% of the total number of establishments (Figure 41.1); small companies with 18–24 employees representing 30.73%; medium-sized enterprises employing 25–54 people representing 9.24%; and finally large establishments with a workforce of more than 55 employees representing 8.52% of the total.

Figure 41.1 In Mexico, there are many family businesses making bakery products. This is a handmade process.

It is estimated that approximately 450 000 people are working directly in the bakery industry, generating more than 1 million indirect jobs.

Promotion and product innovation have boosted sales of the bakery sector, but sales are also influenced by climatic conditions – rain and cold weather make consumers demand more products.

More than 80% of the total number of establishments bake traditional bread and cake, so the industry has an enormous influence on the Mexican economy. Prices for breads and cakes are

atypical because their price is stable regardless of whether the volume of sales goes up or down, probably due to Mexican people's habit of consuming bread and cakes for all types of celebration. In fact, per person, the annual consumption of flour bread and sweet derivatives is 32.5 kg.

The baking industry is one of the most productive food industries in Mexico, and it is continuously consolidated as new products are introduced to reflect the changing eating habits of the population, without losing the products' handmade and traditional Mexican essence.

In Mexico, 90% of the people consume sweet and white bread (bolillo and telera). The national chamber of bakery and related industries (Cámara Nacional de la Industria Panificadora CANAINPA), founded in 1945, has 29 offices in various states and 26 500 partners countrywide. The consumption of bread per person in Mexico decreased due to the economic crisis and the increase in the price of the products. In 1999, the market for packed bread was worth around US$300 million. Recently, the bakery industry of Mexico had sales totalling around US$10 000 million. The bread produced in small factories (artisanal bread) is approximately 80% of total production in the country, industrial bread (big factories such as Bimbo) is 12%, and other factories (supermarkets) are 8%. During 2010, the industrial sector of the Mexican bakery industry reported the production of 539 989 tons of bread (sweet and white). Mexican entrepreneurs founded Group Bimbo in 1945, and today it is the biggest single bakery industry worldwide based on trademarks, production volume, and sales. Group Bimbo has factories in 17 countries, with 7000 products and 150 trademarks. The increase in sales of Group Bimbo is due to the research and development of new products, but the success is attributed to good distribution because customers can always buy fresh products. In Mexico, Group Bimbo has 24 factories that produce bread (sweet and salad) and 6 factories that produce cookies and small cakes. Group Bimbo has 23 factories in Central and South America, and 34 factories in the United States. Another factory is located in Beijing, China. In 2010, Group Bimbo made sales of around US$6 million in Mexico.

Major types of bakery products

The influence of the French people is valid, because in some regions of Mexico white bread or salt bread is named French bread, and in other regions this kind of bread is called bolillos, teleras, or baguettes.

Bread is a very popular staple in the Mexican diet due to the wide variety of types, easy digestibility, exotic taste, and attractive colors and shapes. Mexican breads from different regions are listed in Table 41.1 with their Spanish names and their main characteristics and ingredients to demonstrate the visual characteristics that are sometimes similar to breads from other regions of the world. Some examples are shown in Figure 41.2. Important characteristics of Mexican bread are its crispy texture, variety of flavors, and uses. Mexican people consume bread daily and even at special parties–bread in Mexico is part of the culture and traditions. Reportedly, there are approximately 1600 types of Mexican bread, therefore Mexico may have the highest number of bread types in the world. This huge diversity of bread is due to regional cultures such as "nahua", "tolteca", "zapoteca", "mixteca", "otomi", "tzetzal", "sotzsil", "mayos", "mayas", "tarahumaras", "huicholes", each supplying diverse bread types. Each state, county, and small town have their own bread; for example, in some small towns in diverse states such as Tingüiidin in Michoacan, Acámbaro in Guanajuato, Chilapa in Guerrero, and San Juan Huactzingo in Tlaxacala, the main economic activity is making bread.

Table 41.1 Some characteristics of Mexican bread from diverse regions

Name	Region	Ingredients[a]	Characteristics
Chilindrina	All country	Cinnamon	Cover with small balls of brown sugar and cinnamon
Conchas	All country	Butter, vanilla or chocolate flavoring	Cover with rectangular crusts of butter with sugar to form shell
Empanochada	Chilapa, Guerrero	Molasses	Some pieces of molasses are in the inner. Brown color
Coyotas	Sonora State	Brown sugar	Circular flat bread with two layers stuffed with brown sugar
Cemitas	Puebla State	Sesame	Bread: crisp, large, and decorated with sesame seeds on top, filled with cooked ingredients
Almohadas	Zacatlan, Puebla	Cheese	Rectangle bread stuffed with cheese and sugar
Bread of cream	Guanajuato State, Tlaxcala State	Cream	Soft bread with cream added to the other ingredients
Tepopoztes	Colima State	Corn flour, butter, brown sugar, anise, cinnamon.	Cornmeal muffins

Pan of pulque	San Luis Potosi State	Pulque	Pulque as the yeast used to make bread volume and body
Cocol	Hidalgo State	Sesame	Before it is baked, the mass is given the figure of a rhombus
Sweet bean pie	Baja California State	Beans, clove, brown sugar, cinnamon	Pie stuffed with beans, clove and cinnamon
Chorreadas	Saltillo, Coahuila	Brown sugar, cinnamon, nut	Bread stuffed with brown sugar, cinnamon and nut, baked in the oven
Tureletes	Chiapas State	Toasted rice flour, cinnamon, cheese	Bread: diamond-shaped with light golden color.
Pumpkin pie	Durango State	Pumpkin	Pie filled with pumpkin
Marquesote	Oaxaca State	Maize starch	Porous bread
Milpa bread	Yucatan State	Beans, pumpkin seeds	Bread stuffed with beans and squash seed paste wrapped in banana leaves
Coricos	Sinaloa State	Maize flour	Bread made of corn flour and donut-shaped
Campechanas	México city	Puff pastry	Rectangular bread of puff pastry with sugar sprinkled on
Panetela	Tabasco State	Milk, lemon peel	Rectangular bread of compact crumb
Apasteladas	Veracruz State	Lemon juice	Rectangular bread stuffed with curd and sprinkled sugar on
Peanut polvoron	Zacatecas State	Peanut	Circular bread of peanut with icing sugar sprinkled on
Tlaxcales	Tlaxcala State	Corn grains, lemon or orange peel	Bread baked in the oven, circular shape

[a]In addition to wheat flour, water, bakery yeast, salt, and sugar.

Figure 41.2 Some examples of the diverse forms of Mexican breads (clockwise): orejas, magadalenas, polvorón, moño, cuernos, concha.

There are two main types of Mexican bread: sweet and salt. The sweet bread type includes 1200 varieties and the salt bread type 400. Bread production in Mexico is mainly at the artisan level, with the bread prepared early in the day, baked, and distributed to the local market in small vehicles or on foot (Figure 41.3) in the street, with the seller calling loudly. Some supermarkets have a bread making area with a gas oven. Supermarkets also prepare bread early in the day because people buy bread for breakfast, usually salt bread also known as pan de labranza (bolillo, telera). In a significant number of cities and towns, bread is preferred for breakfast. Many people in Mexico have a small breakfast of sweet bread with hot chocolate, milk or coffee, before the start of their daily activities. Afterwards, around 10:00 am, they have a big breakfast that includes fruits, juices, eggs, refried beans, hot sauce, and pan de labranza. Other people and many schoolchildren prefer a food know as "torta" (similar to a sandwich), that is prepared with fresh bolillo or telera. These breads are cut down the middle (Figure 41.4) and butter or mayonnaise is spread on each half. One half is then filled with refried beans, pickled jalapeños, avocado, tomato, onion, lettuce, and the main filling of jam, chicken, sauce, fried egg, or cheese. This is topped with the other half of the bread. Torta is considered a complete breakfast food.

Figure 41.3 A typical method for distributing bread during the morning.

Figure 41.4 Torta is a typically food for children.

The following sections describe the main types of Mexican breads.

Bolillo, telera or birote

The generic name is pan de labraza, but depending on the region of the country it may also be called bolillo, telera or birote. Pan de labranza is probably the most popular and recognizable Mexican bread. Bolillo is probably the most popular name of this salt bread, and its texture and taste depend on the region of the country from where it is produced. Pan de labranza from diverse regions of Mexico with the original name is shown in Figure 41.5. As most production occurs in small establishments named panaderías, the bread's characteristics have been conserved from generation to generation without appreciable changes. Bolillo is fermented bread made with wheat flour, salt, sugar, water, and fresh yeast; small variations can be found with the addition of milk and oil. When the dough is ready, small pieces are cut and extended over an aluminium tray and a small groove is made with a thin piece of wood. The bolillo is baked, producing a thick and crunchy crust. To develop new bolillos, Mexican bakers have been producing formulations that include chilli, because it is a tradition in Mexico to eat very spicy dishes. Other formulations include bolillo with cheese, which is ready to eat or is used to prepare a torta.

Figure 41.5 Depending on the region, bread has different names such as bolillo, telera, birote, or micha.

Concha

The concha is perhaps the most traditional sweet bread of the Mexican bakery. Usually, a piece of concha can be found in a small basket on the table of each Mexican family during breakfast and dinner, when it is traditionally consumed with hot chocolate, dipping the concha in the liquid. This sweet bread is very attractive due to the diversity of color such as

chocolate, white, yellow, and pink. The formulation to make concha includes the additional ingredients sugar, butter, and eggs, to produce a soft and spongy texture that is unique to this bread. When the dough is ready, a small piece is taken by hand, covered with a sweet paste made with various flavors, and a mold used to mark the shape of a shell.

Sweet breads

Mexican bakers are very creative, and there are different and novel sweet breads, with shapes, sizes, flavour, texture and colors, elaborated daily with diverse ingredients (Figure 41.2). Additionally, the country has 32 states, provoking great diversity of bread. This large number of Mexican sweet breads has a great diversity of names, for example, chilindrinas, borrachitos, garibaldis, orejas, puerquitos, picones, cocoles, morenas, cuernos, corbatas, trenzas, pellizacadas, polvorones, ojo de pancha, trompadas, ojos de buey, hebillas, empanochadas, cemita, rascabuches, pulgas, pan piedra, caracoles, pechugas, pelucas, camellias, zapotes, payados, grajeados, volcanes, tortugas, mamones, campechanas, chamacos, huaraches, nopales, regañadas, ladrillos, pan de yema, pan de agua, coyotas, aguacates, and so on. The list is huge and each region or, more commonly, each baker gives name for new breads. The diverse ingredients used for the production of sweet breads and their characteristics are shown in Table 41.1. Different regions of the country have specific breads that are consumed widely, in addition to the traditional Mexican breads such as conchas, cocoles, trenzas, and so on.

There is special bread elaborated with pulque. Pulque is a traditional Mexican beverage made by fermenting the sweetened juice obtained from different species of maguey (*Agave americana, A. atrovirens, A. fierce, A. mapisaga, A. salmiana*). This drink is consumed by indigenous and mestizo populations in many regions, particularly in central Mexico (Godoy and others 2003).

The native Mexican people were making pulque before the arrival of the Spanish. Pulque was considered to be the beverage of the Aztecs gods and was consumed by the Aztec kings. Pulque bread was first produced in the north of Mexico (Saltillo, Coahuila) in 1925, and is now prepared in various regions due to its special taste and flavor (Figure 41.6). The Tlaxcala people knew the mass of wheat flour, which allowed them to develop different figures, using pottery techniques. Making bread integrated such cultural forms as the transposition of ceramic techniques and the use of xaxtle (sediment of pulque) and pulque. Fermentation with pulque produces "bread of pulque", which is currently mainly produced in Tlaxcala and Hidalgo, as well as in other areas of the country that were colonized by Tlaxcala's people, such as Querétaro, San Luis Potosi, and Coahuila (Barros and Buenrostro 2004).

Figure 41.6 Pan de pulque.

Bread festivals

Mexico is known for its traditions, which are usually commemorated with local, regional, and national festivals. Some breads (mainly sweet bread) are made specifically for these events. Various festival breads from different regions of the country are shown in <u>Figure 41.7</u>.

<u>**Figure 41.7**</u> Different types of bread are produced for various special events (top to bottom, right to left): rosca de reyes, pan de feria, pan de fiesta, pan de navidad, pan de muerto, pan de feria.

Fair bread

People transport their oven, mixer, showcase, and so on, in trucks to where a festival is being held. They make the fair bread and set up a small store in the street of the festival town or city. These breads show colorful, diverse flavors with nuts, vanilla, and cream. Some breads have starchy fillings of different colors. Fair bread has a soft texture and a sweet taste. The families that attend the fair buy this bread because it is not produced at other times of the

year. Usually, the production of fair bread is a family business which travels across the country looking for local and regional festivals.

Pan de Muerto

The most important and traditional holiday of the country is Día de los Muertos (day of the dead). Many families meet on these dates (1st and 2nd November) in the cemetery to celebrate, because the belief is that the souls of the dead come back to be with family to enjoy the diverse traditional dishes that are made only during this season of the year, for example mole verde, tamales, pipipollo, as well as some candies and desserts. Día de los Muertos is a happy and colorful celebration; the people adorn the graves with many flowers and other artistic pieces, and families take the dishes and beverages (including mescal and tequila) to the cemetery to eat with the dead. Usually, the preferred dishes, desserts, and beverages of the dead are prepared and consumed. Other families prepare an adorned table or "altar" with flowers, candles, paper ornaments, dishes, beverages, candies, fruits, and pan de Muerto in the house. The family members consume all the food. Pan de Muerto is a traditional bread that is prepared specially for this celebration with different shapes, sizes, and decoration. It is sold extensively because most Mexican people consume this product during this holiday.

Rosca de Reyes

The tradition of the Rosca de Reyes was imported from southern Europe to commemorate a catholic tradition that shows the gifts granted to the baby Jesus, which were mostly dried fruits, wheat flour, nuts, honey, and eggs. These items were used to prepare a circular bread to represent a crown. Some small plastic baby figurines are hidden inside the Rosca de Reyes to represent a chapter of the bible. On 6 January, families and friends, as well workers in offices, meet to share the Rosca de Reyes and eat it with hot chocolate. The people who find the plastic figurines have to host a party on the 2 February, traditionally known in Mexico as "Día de la Candelaria". This bread is made throughout the country and a significant amount of Rosca de Reyes of different sizes is sold, conserving this tradition.

Mexican wheat varieties

The cultivation of wheat arrived in Mexico with the arrival of the Spanish people, but the extensive knowledge of the Indians about growing plants improved the cultivation of this cereal; however, the cultivation of maize was higher than wheat as maize was used by the Indians as tribute to the gods. However, they learned not only how to sow wheat, give it the care necessary for growth, thresh it, clean it, and store it, but once they obtained the grains, they also learned how to grind it to get flour.

The classification of wheat varieties in Mexico, which is based on its gluten properties, is different to the classification used in United States and Canada, which is based on its growing characteristics. The classification of Mexican wheat varieties is shown in Table 41.2; groups 1 and 3 are in the highest demand for industrial purposes. However, the demand for the crystalline wheat type has recently increased. In Mexico there are two cycles of harvest for wheat: fall–winter and spring–summer. In the first cycle, the seed is planted in fall; the plants emerge in winter to grow slowly and are harvested in spring. The wheat planted in spring–summer grows fast and continuously and is harvested in summer. The average yield of Mexican wheat has increased from 740 kg/ha in 1940 to 4480 kg/ha in 2004. This increase was due to diverse factors, but the main factor was the development of new improved varieties. The first approach for the genetic improvement of the wheat was to increase the yield and range of environmental adaptation. Nowadays, the objective is to combine the genes associated with high yield, resistance to diseases, stress tolerance to diverse environment factors, and industrial quality of the grain. Two research institutions in Mexico (Centro Internacional de Mejoramiento de Maíz y Trigo (CIYMMYT) and Instituto Nacional de Investigaciones Forestales Agrícolas y Pecuarias (INIFAP)) are working on the improvement of industrial quality wheat, identifying the gene combinations and proteins that will provide the quality characteristics required by the bakery industry. This knowledge is being used to develop new wheat varieties in Mexico (Espitia-Rangel and others 2003, 2004).

Table 41.2 Mexican classification of wheat on the basis of the properties of the gluten of wheat

Wheat	Gluten type	Texture of grain/endosperm	Uses
Group 1	Strong (very stretchy) and extensible; hard to semi-hard	Hard to semi-hard	Mechanized industry baking, mainly producing flour for bread box; breeder of weak wheat
Group 2	Medium strong (stretchy) and extensible	Hard to semi-hard	Handcrafted or semi-mechanized bread; breeder of weak wheat or wheat with very strong gluten
Group 3	Weak (slightly stretchy) and extensible; soft	Flour not used in baking; requires mixing with group 1 and group 2 wheat	Cookies and tortillas, fritters, and others: can be used in artisan bakery; corrector of wheat with strong gluten
Group 4	Medium and tenacious (not extensible)	Hard to semi-hard.	Not possible to bake bread with the flour because of high tenaciousness; mixed with strong wheat for pastries (pastry and cookies) industry
Group 5	Strong, tenacious, and short (not extensible)	Very hard and crystalline; endosperm has a high content of yellow pigment (carotenoids)	Not useful for baking; pasta (spaghetti, macaroni, dried soups, etc.).

The national production of wheat is concentrated in 6 of the 23 states (around 85%): Sonora (35%), Guanajuato (17.5%), Baja California (11.5%), Sinaloa (9.2%) Michoacán (6.4%), and Jalisco (4.4%). The total production of Mexican wheat in the decade 1991–2000 was 35.7 million tons. There are two regions: the Northwest supplying 55% of the national production and Bajio supplying 28%. The average harvested area in the 1990s was 898 000 ha. The planted area decreased at a rate of 3.6% per year due to negative changes in the fall–winter and spring–summer cycles. Of the total harvested area (898 000 ha), 73% is under irrigation. In the same decade, the planted area grown under temporal (rain fed) conditions decreased by around 51 000 ha, indicating an annual average decrease of 2.8% due to climatic problems.

There are wheat varieties that are adapted to the two main regions. In Bajio, the variety Salamanca S75, which was commercialized in 1975, produces a high economic impact, as it has a high yield and resistance to regional pests and was preferred by producers in Guanajuato until the 21st century. Salamanca S75 has been the most important improved variety in the Bajio region as its milling quality is good even when it is blended with other varieties and it satisfies the needs of the Mexican bakery industry. The yield of Salamanca S75 is very high compared with other varieties (Toluca F73 and Yécora F70) released previously. During the 1980s, over 160 000 ha of Salamanca S75 was planted, corresponding to 90% of the total area harvested in Bajio (Guanajuato, Michoacán, and Jalisco).

Consumption of bread in Mexico

Usually, Mexican bread is consumed immediately after its preparation, so preservatives are not used in its production, except in those factories that package and distribute the bread in some regions of the country or nationwide. Clearly, Mexican people prefer fresh bread because long queues form in panaderías to buy the bread immediately after baking; this is a tradition in our country. In Mexico City, buying bread in the afternoon is a daily activity, because fresh or hot bolillo and teleras are produced ready for dinner. There is a proverb that says that the boys ask the girls: "At what time you are buying the bread?" so they can talk with the girls whilst walking to the store in the afternoon.

Final remarks

Mexico is a very big country and so there is a high diversity of bread. The Mexican bread industry is artisanal as the factories are small and knowledge is passed from generation to generation. The two main types of bread produced are salty bread and sweet bread, and they are eaten immediately after baking. A wide diversity of shapes, colors, taste, and texture are found in Mexican breads. Various types of bread such as pan de muerto and rosca de reyes are produced on special dates. There are breads that are produced in specific regions such as pan de pulque and coyotas. The Mexican bread industry constitutes an important part of the country's economy, and the diversity of Mexican breads promotes its incorporation into the diets of other countries such as the United States and Spain.

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Bakery Products of Turkey

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Introduction

Turkish cuisine is full of some amazing food components with which to spoil your taste buds. However, no matter where you go in Turkey and whatever it is that you eat, you will find one thing to be a constant part of the meals, and that is bread. Eating Turkish bread is not restricted to breakfast as it is eaten with all meals at all times of the day, therefore almost every household either bakes its own bread or sends its dough to a communal bakery. Baking bread is such an integral part of Turkish lifestyle that every household must have its own expert baker. The foundation of Turkish food is, if anything, dough made of wheat flour. The original white bread that is used in Turkey is called ekmek and flat bread is known as pide. There are other types of breads such as simit, which has sesame seeds, and manti that has very much in common with ravioli. In fact, there is a whole family of foods that are made out of these breads and categorized as "borek". These breads are eaten for breakfast, for snacks, and they also accompany most of the daily meals. These very versatile pieces of bread can be sliced, filled, fried, baked, toasted, grilled, and prepared in many inventive ways. The Muslims of the Ottoman period believed that bread was one of the earliest forms of cuisine dating back to the time of Prophet Adam, and bread is still held as one of the simplest and most honorable foods to eat. Taking their inspiration from this very basic food, they made bread a big part of their daily lives. Some would argue that there is no bread on Earth that tastes like Turkish bread, and you have to eat it to realize how good it actually is (Kwintessential 2012).

Turkish bread transcends all social classes and is enjoyed by the rich and the poor alike. It is therefore no surprise to find that bakeries are quite busy throughout the day trying to produce enough bread for the whole community. As a result, the aroma of sweet bread fills the streets and almost hypnotizes people passing by, persuading them to enter a bakery. It is noticeable that many people bring their bread home with the crisp ends missing because they just could not resist nibbling on the bread on their way home. Some breads must be consumed the same day they are baked, for example ekmek, simit, and pide. The Sunday treat is usually Manti dumplings of dough with a special meat filling. Then there are those breads, like borek, that are reserved for special occasions. These can be relatively difficult to make and are not a job for the amateur baker.

Bread is one of the oldest foods. Evidence from 30 000 years ago in Europe has revealed starch residue on the rocks used for pounding plants. It is possible that during this time, starch extract from the roots of plants such as cattails and ferns was spread on a flat rock, placed over a fire, and cooked into a primitive form of flat bread (Foodtimeline 2012). Flat breads are produced in most parts of the world, and in Turkey, the Middle East, and Northern African countries they are usually made using traditional methods. Flat breads comprise either one (single) layer or two (double) layers. Another two sub-groups for single layered flat breads are leavened or unleavened. Two-layered flat breads are leavened. The most significant difference of flat breads from other loaves is that they have lower specific volumes. The main ingredients used in flat bread production, the production steps of flat bread, the various types of flat breads produced all over the world, and the production methods for the most common Turkish flat breads are all discussed in this chapter (Gocmen and others 2009). The use of the tandoor oven is popular in Turkish bakery and also in Iran, Pakistan, and India ([Figure 42.1](#)). The development of the Chorleywood bread process in 1961 was a major production advance which used the intense mechanical working of dough to

dramatically reduce the fermentation period and therefore the overall time taken to produce a loaf. This process incorporates high-energy mixing that allows lower protein content grain to be used, and is now widely used around the world in large factories. As a result, bread can be produced very quickly and at low cost to both the manufacturer and the consumer.

Figure 42.1 The tandoor oven (Photo: Anonymous).

Turkey has the highest bread consumption in the world with about of 200 kg consumed per person (2006 estimates; Bugday 2012). An average number of 82 million pieces of bread is produced, 77.34 million being consumed, and 4.6 million wasted for various reasons (Bugday 2012; Sabah 2012). In Turkey bread is usually made from wheat; however, where wheat is scarce and expensive, barley, corn, and rye flour are mixed to make bread. In Turkey, bread types can be divided into two groups:

- leavened style
- Unleavened style.

Leavened bread

Leavened bread contains a leavening agent, usually yeast. Leavened bread is soft, light, and fluffy in texture, and contains tiny air pockets like a sponge. The leavening agent mixed into the bread dough causes the dough to rise both before it is baked and during baking. A simple leavening technique for bread involves the use of gas-producing chemicals, and there are two common methods. The first method uses baking powder or self-raising flour that includes baking powder. In the second method, baking soda is added to an acidic ingredient such as buttermilk, which reacts with the soda to produce gas. In Turkey, many different types of leavened bread are made, such as:

- bazlama (bazlamaç, bezdirme, bezirme)
- dari bazlama
- ebeleme
- fodla
- gilik
- gömeç
- gübaye
- halka
- kakala
- kalin
- lavaş (lavaj ekmeği)
- mayali (mayali sepe)
- pit-pit
- pobuc
- sac ekmeği
- sac arasi ekmeği (iki sac arasi)
- tandir ekmeği
- taşli firin ekmeği
- tepsi ekmeği
- yuvarlak
- simit.

Bazlama (bazlamaç, bezdirme, bezirme) is a Turkish bread type, is defined as a single-layered, flat, circular, and leavened bread with a creamy yellow colour. It bears a close resemblance in taste to English muffins and has an average thickness of 2 cm, with diameters ranging from 10 to 25 cm. It is a very popular flat bread made from wheat flour, drinking water, table salt, and yeast. After 2–3 h fermentation, 200–250 g pieces of dough are divided,

rounded, sheeted to a desired thickness, and baked on a hot metal plate (sac in Turkish). The bread is turned over during baking to bake the other side. It is generally consumed fresh straight after baking. The shelf-life of bazlama varies from several hours to a couple of days depending on storage conditions (Başman and Köksel 1999).

Dari bazlama is a type of flatbread composed of leavened dough with a 1–1.5 cm wide opening, cooked on a hot metal plate. Dari Bazlama is prepared with wheat flour, corn flour, millet flour, salt, water, and sourdough (Tekeli 1970).

Ebeleme is made from a leavened dough sheet which is baked on a hot metal plate. After cooking, a top and bottom portion of dough is greased. This bread is made in the area of Ankara (Tekeli 1970).

Fodla (an Arabic name) is a similar kind of pita bread that is produced from whole wheat flour (Oğuz 1976).

Gilik is made with crepe-like dough in the Black Sea region (Oğuz 1976).

Gömeç – in great feasts, gömeç breads carry a deep and important social meaning in Anatolia. Usually around 50 or more pounds of dough is buried under hot ash and cooked. The dough is divided into pieces of the desired size and the separated pieces are baked on metal legs in the oven (Tekeli 1970).

Gübaye is specific to the Siirt region, and is baked in a tandoor (Koşay and Ülkücan 1961).

Halka is a bread type in the shape of ring made from leavened dough (Ongan 1958).

Kakala is a circular lump of leavened dough which is cooked in a so-called stone pit. It is made in the Artvin province (Tekeli 1970).

Kalin is made with leavened dough. Dough pieces of approximately 500 g are spread out 2 cm thick and then cooked in a tandoor. It is specific to the Kars region (Tekeli 1970).

Lavaş (lavash bread) is a soft, thin, flat bread popular in several countries of the northern parts of the Middle East. Traditionally the dough is rolled out flat and slapped against the hot walls of a clay oven. While quite flexible when fresh, lavaş dries out quickly and becomes brittle and hard. The soft form is easier to use when making wrap sandwiches; however, the dry form can be used for long-term storage and is used instead of leavened bread. It is also known in English as lavash or cracker bread. Dry left-over lavash is used to make quick meals after being re-hydrated with water, butter, and cheese. Lavash bread is also used with kebabs to make dürüm wraps. Lavash is made with flour, water, and salt. The thickness of the bread varies depending on how thinly the dough is rolled out. Toasted sesame seeds and/or poppy seeds can be sprinkled on before baking. In the Sivas region, lavash is baked in kilns (Tekeli 1970; Demiral 1968).

Mayali (mayali sepe) is a type of leavened bread (1 cm thick and 10–15 cm in diameter) which is usually cooked in a sac. In some areas, it is cooked in an oven (Tekeli 1970).

Pit-pit is made with leavened dough. It is usually round or can be baked in other desired shapes and in various sizes. After fermentation, it is cooked in an oven. It is made in the Çorum area (Barin 1982).

Pobuc is prepared by making a 15–20 cm wide, thick, round shape of leavened dough which is glued to a tandoor and cooked (Tekeli 1970).

Sac ekmeği (sac bread) is called the 'open bread' in Sanliurfa city of Turkey. The dough is baked on a sheet of metal and is fermented up to 2–3 mm thick, and may be an ellipse or circle (Tekeli 1970).

Sac arasi ekmeği (sac arasi or iki sac arasi bread) is also called kastra. It is prepared like sac bread but it is a little bit thicker. Prepared dough is placed on the hot sac then cooked with burning ash and a red-hot sac (Tekeli 1970).

Tandir ekmeği (tandir bread) – the tandoor can be defined as a type of oven that is made by digging a hole in the ground. Tandoor bread is made within a recessed tandoor. A fire is lit on the floor of the tandoor and the walls are heated up. If the dough can stay on the wall of the tandoor without falling off, it means that the tandoor bread is ready to eat (Ongan 1958; Halici 1979).

Taşli firin ekmeği (taşli firin bread) – is made with a mix of flour, water, salt, and yeast that is kneaded and then fermented. A lump of dough is then hand rolled and allowed to ferment for a second time. An oven is lit and pebbles are thrown in. The fire heats these stones up and the prepared dough is cooked by throwing it on the hot stones. This type of bread is made in the Malatya area (Tekeli 1970).

Tepsi ekmeği (tepsi bread) is made from leavened dough placed on an oiled square pan and cooked in the oven. This bread is made by Balkan immigrants living in Nigde. In the Aydin region, it is made with chickpeas (Halici 1981).

Yuvarlak is made with leavened bread dough, and is prepared in a pan from a strip of dough approximately 10 cm wide and 20 cm long. Sesame and poppy seeds are spread on the bread. It is placed in a low-heat oven in the evening and cooked until morning. It is soaked in water before eating (Halici 1983).

Simit is a circular bread with sesame seeds ([Figure 42.2](#)). It is very common in Turkey as well as in Greece, Serbia, Bulgaria, and other parts of the Balkans, and in the Middle East such as Lebanon. The size, crunchiness/chewiness, and other characteristics of simit vary slightly by region. In the city of İzmir, simit is known as "gevrek," (literally "crisp" in Turkish), although it is very similar to the Istanbul variety. Simits made in Ankara, the capital of Turkey, are smaller and crisper than the ones in other cities. Simits in Devrek/Zonguldak are made with molasses, and in common with Eskişehir province, no sesame is used.

Figure 42.2 Simit (Photo by Seyhun Yurdugül).

Drinking Turkish tea with simit is traditional in Turkish culture. Simit is generally served plain, or for breakfast with tea, jelly, jam, or cheese. Simit and koulouris are often sold by street vendors, who either have a simit trolley or carry the simit in a tray on their head. Street merchants generally advertise simits as fresh ("Taze simit" /"taze gevrek") since they are baked throughout the day. Simit is also known as "Turkish bagel" in the United States.

Boyoz is a bakery product, also known as 'fatty flour', which is special to İzmir but is not generally known in most parts of Turkey. It was first introduced to İzmir cuisine by the settled 'Sefarad' Jewish community, comprising immigrants from Spain after 1492. In countries with a strong Spanish culture, such as Argentina, Chile, Peru, Mexico, and especially in the Sefarad population, the types of boyoz made with cheese and spinach are intensively prepared and consumed. Initially dough is kneaded into a ball and rested for around 2–3 h in a pan. The dough is then spread into a plate-shape and rested for a while, and then by shaking in the hand, is spread out again, rolled, and rested for a further 1–2 h. In order to serve small pieces of bread, the dough is first put on a tray and cut into small balls, and allowed to rest in a vegetable oil and tahin mixture for about 30 min to 1 h. Before baking at a very high temperature, some desired extra ingredients such as cheese, spinach, or minced meat can be added inside the tiny and neatly opened mille-feuille-style yufka, but the traditional boyoz is plain. This plain version of boyoz dough always comprises flour, sunflower oil, tahin mixture, and salt (Izmirnews 2012).

Lokma is famous in İzmir. The yeast-containing dough is put into hot oil, removed, served by

pouring sugar solution (sherbet) over it, and consumed as a dessert. It is prepared using two glasses of flour which are put into a bowl and mixed with powdered sugar. The instant yeast is mixed with water and milk, and poured into this bowl by opening the middle of the dough, like a pool, after cooling. Then melted butter and egg white are added to the middle to obtain softened dough. The melted butter is then transferred to a pan and the dough is fried, and removed with a spoon. For preparing the sherbet, four glasses of powdered sugar and 2.5 glasses of water are boiled and cooled down. The lokmas are dipped into this cooled sherbet and served hot after mixing for a few minutes (Izmirnews 2012).

Borek (burek) – burek, börek, byrek, boeregs, byurek, boureki, bourekas, "çibörek" or brik, are names for the same products (Figure 42.3). It is popular in many countries making up the former Ottoman Empire. There are, however, variations as far afield as Tunisia and Algeria and it has even been related to Indian samosas and Chinese spring rolls. This shows that there are few cultures able to resist flaky pastry stuffed with delicious sweet or savory fillings such as cheese, spinach, minced meat, or other ingredients (Blog.travelpod 2012; Burek 2012).

Figure 42.3 Burek (Photo by Seyhun Yurdugül).

Açma (achma) is another common bakery product of Turkey (Figure 42.4). Initially a small 'crater' of sieved flour is formed and then salt, powdered sugar, yeast, and sunflower oil are added. Half a glass of warm water is added, and the yeast is melted by hand. Some flour is added to this mixture which is then rested for 3–5 min. The dough is kneaded with an appropriate amount of warm water. After picking and rolling lemon-sized pieces from the dough, it is rolled out to approximately 12 × 8 cm, a spoonful of margarine is spread inside, then it is rolled and coiled around to make spherical pieces. These are put on to an oiled tray and the açma is allowed to swell by the yeast action under the mild conditions of room temperature. The fermentation time of the dough depends on the ambient air temperature. Egg yolks, whipped with vegetable oil, are spread onto this mixture and some black cumin seeds are added. These açma are baked in a previously heated oven until the top layer is brown. For a different taste, margarine and a spoonful of olive paste, can be spread inside the dough to form an 'olive Açma' (Oktayusta 2012).

Figure 42.4 Achma (Photo by Gözde İnan).

Poğaça (pogacha) is a bakery product generally found in Serbia, Croatia, Turkey, and Macedonia ([Figure 42.5](#)). It is similar to Italian vienna bread in texture and flavor and there are as many recipes for it as there are shapes. This "one-rise" recipe is used to produce a round loaf. The production is carried out by adding hot milk to butter, allowing it to cool to lukewarm, and then adding yeast and sugar. This mixture is stirred until it is dissolved. Five cups of flour are added into the bowl of a standard mixer fitted with the paddle attachment. The milk–yeast mixture, sour cream, oil, egg, and salt are added to this bowl, and it is mixed well. After changing the paddle to a dough hook, the mixture is kneaded on medium-low for about 5 min, or until the dough is smooth and elastic. The dough is then turned out into a large greased bowl. The dough is flipped over to grease both sides, covered and allowed to rise until the size has doubled. The dough is then flattened and placed in a 10-inch round greased pan with high sides (about three inches high), or shaped by hand into a 10-inch 'round' and place on a parchment-lined baking sheet, before baking in a pre-heated oven at 350 °F. Using a sharp knife, the top of the dough is given a shallow cut three times. Baking time is about 1 h or until an instant-read thermometer registers 190 °F, after which it is removed from the oven and placed on a cooling rack (Easteuropeanfood.about 2012).

Figure 42.5 Pogacha (Photo by Seyhun Yurdugül).

Unleavened bread

Unleavened bread is made by mixing together salt, water, the variety of flour, and then kneading and shaping with a rolling pin. Examples are:

- bazlama (unleavened type)
- fetil
- güdül
- gartalaş
- gözleme
- kömeç (kömme, kömbe)
- misir ekmeği
- ter ekmeği
- yufka.

Bazlama (unleavened type) is prepared with water, salt, and flour, and a very thin sheet of dough is baked on a metal sheet. In some areas the dough sheet is prepared a little thicker. In Adiyaman, Malatya, and the Trabzon regions, it is called tablama. Unleavened bazlama is called göbü in Zonguldak-Çankiri; in İzmir it is the so-called bezdirme (Halici 1981, 1983).

Fetil is a type of bread which should be eaten fresh. This bread is made smaller, and is also thicker, than if it were made from a very thin sheet of dough, and is baked on a metal sheet. It is made with whole wheat flour, giving it a more delicious and nutritious taste. This type of bread is specific to Sivas-Elaziğ areas (Uçer 1992).

Güdül is prepared with corn flour or wheat, and baked on a tandoor or metal sheet. It is known from the provinces of Samsun, Sivas, and Tokat (Oğuz 1976).

Gartalaş is made from a very thin sheet of unleavened dough. It is well known in Bolu, Eskişehir, and the Bursa areas (Oğuz 1976).

Gözleme is a savory, traditional Turkish, hand-made and hand-rolled pastry (Figure 42.6 and Figure 42.7). Fresh pastry is rolled out, filled and sealed, and then cooked over a griddle. The name derives from the Turkish word göz meaning 'eye'. Traditionally, it is baked on a sac. Gözleme varieties include pastries with a mix of spinach and feta cheese; or spinach, feta cheese, and minced meat; and spinach, feta cheese, and egg. There are also pastries containing individual ingredients such as seafood, egg, minced meat, cheese, potatoes, and mushroom.
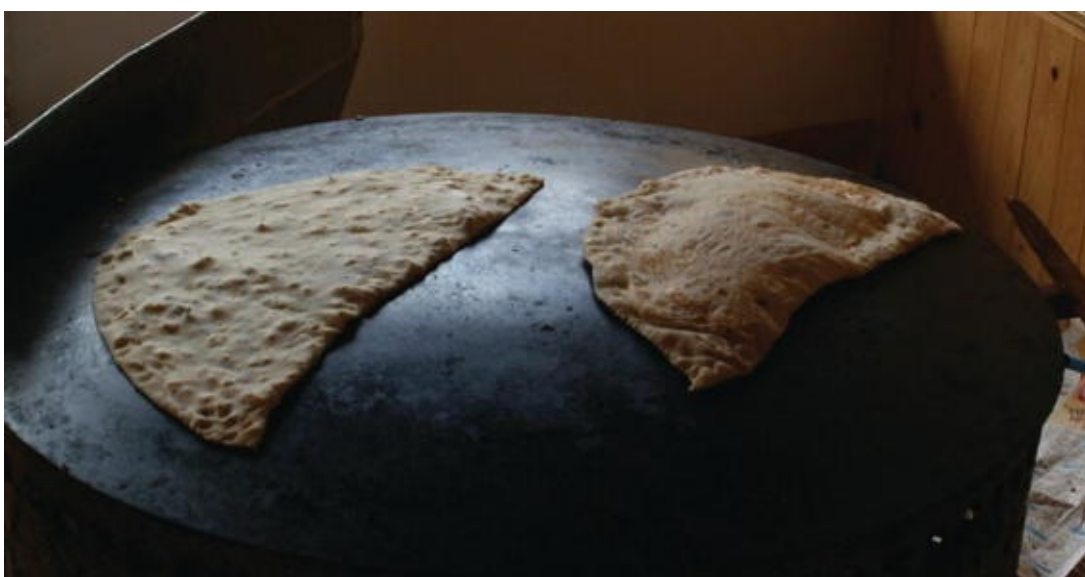
Figure 42.6   Gozleme on the sac (Photo by Gözde İnan).

Figure 42.7 Gozleme (Photo by Gözde İnan).

Kömeç (kömme, kömbe) is unleavened bread cooked on coals and is from Trabzon and Zonguldak. In the Zonguldak areas, kömeç is made without salt. In the Balikesir area, it is known as kömme. In many parts of Anatolia, it is made as a kind of ash pita which can be either leavened or unleavened, and containing fat or fat-free (Üçer 1992).

Misir ekmeği (corn bread) is usually made in the Black Sea region. As one of the principal crops of Turkey (more than 2 million tons of production a year), corn is used for fermented and unfermented bread-making in various regions of the country. The dough includes water, corn flour, and salt without yeast. Corn bread is cooked on a metal sheet or on a baking pan in the oven. If eggs are applied over the bread, it is called corn bread with eggs, and of course the color is yellow. Corn bread is made daily for quick staling and crumbling. Corn flour is claimed to contain oleic, palmitic, and stearic acids. Corn bread is known as toraman in the Ordu areas (Daglioglu and Tasan 2003; Numanoglu and others 2010).

Ter ekmeği (ter bread) is made from a very thin sheet of dough and cooked fat-free on a metal

sheet. In addition, bandera (dip) is made from this bread. Also, it can be topped with chopped walnuts, closed on the sides, and served in a pan (Tekeli 1970).

Yufka is flat, circular, cream-colored unleavened bread commonly consumed in Middle Eastern countries and is an important bakery product of traditional Turkish cuisine. In some areas, this pastry is called şebit-sepit-şipit. In other areas it is called işkefe-gardalaç. Flours of the wheat varieties Gun and Gerek, and flours of the barley variety Tokak and Gerek bran mixture can be used to produce yufka. A lump of unleavened dough is rolled out to 1–2 mm thickness and up to 50–100 cm diameter with a rolling pin, and baked on a metal sheet. Baking time is approximately 2–3 min. During baking, the bread is turned over once to brown the other side. After baking, yufka bread has a low moisture content and, depending on how low the moisture is, a long shelf-life. Before consumption, dry Yufka bread is sprayed with warm water. The moistened bread is covered with a cotton cloth and is rested for 10–12 min before consumption. In the Ankara-Kirikkale areas, lemon salt, buttermilk, milk, or sour dried fruit pulp of plum are added. In terms of shelf-life, this pastry is the longest-lasting bread (6 months) (Başman and Köksel 2001).

Conclusions and recommendations

Breads made from grains grown in the fertile lands of Anatolia, mainly wheat, form the main staple food item of the Turkish people. Many kinds and tastes of bread are made and shaped by the skilled hands of Turkish people. These breads also contribute to the enrichment of Turkish cuisine as a whole. In addition to the breads, there are many varieties of cakes and pastries that are important in the Turkish diet. Today there are few bread bakers in the cities and so it is difficult to find the sorts of delicious breads that are still made in the villages. Despite this, city dwellers still consider bakery products to be a very important part of traditional Turkish cuisine. As part of traditional local cuisine and to ensure that local food needs are met, home and village traditional bread baking should be encouraged, including the use of the tandoor and cooking on a sac. For this reason, factories already produce flours that give good results for home-baked breads.

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